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THE DIPOLE MOMENT AND CHEMICAL STRUCTURE

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THE
DIPOLE MOMENT
AND
CHEMICAL STRUCTURE

Edited by

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at the University of Leipzig

Authorized Translation by

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PREFACE TO THE GERMAN EDITION

In the summer of 1929 it was again found possible, thanks to support from official and private sources, to hold a conference in Leipzig on a well-defined subject in Physical Chemistry. On this occasion the lectures dealt essentially with the relationships between molecular structure and the magnitude of the electric dipole moment. Owing to the kindness of the publishing firm of S. Hirzel and of the lecturers it has again been possible to make an account of the conference available in book form for a wider public.

Sänger (Zürich) gives an account of his experiments on gases, which (as may be seen by a comparison with the equally remarkable experiments by Zahn (Princeton) and Stuart (Königsberg)) have now attained a high degree of perfection, thanks to the use of the most modern forms of apparatus. The description (illustrated by some fine photographs) of the advances made by Estermann (Hamburg) using the molecular-beam method has also deservedly aroused special interest. Further lectures by Estermann (Hamburg) and by Miss Sherrill, who has been working with Errera (Brussels), deal with the relationships, which have recently been much discussed, between the chemical structure of the molecule and its electrical dissymmetry as measured by the electric moment. The same problem is discussed more thoroughly in the lecture by Ebert (Würzburg), who takes the effect of the mobility of the atoms in the molecular framework fully into account. Light is thrown on the difficult problem of molecular interaction and its relationship to the electric moment in a lecture by W. Hückel (Freiburg) on the dipole moment and the velocity of reaction, written from the chemist's point of view, while Errera (Brussels) in his contribution on the dipole moment and association writes rather from the more usual physical standpoint. An article by K. L. Wolf (Karlsruhe) on the absorption spectra of di-substituted benzenes forms an extension from a novel point of view, not only of experiments on the electric moments of these substances, but also of Hückel's paper. The mobility of the atoms in crystals under electrical forces is dealt with by Errera (Brussels) and Højendahl (Copenhagen); in some respects these papers supplement Ebert's, which seems to deal with quite different parts of the subject. K. L. Wolf (Karlsruhe) discusses the relationships existing between the magnitude of the Kerr effect and the dipole moment, and emphasizes anew how interesting results on the structure and mobilities of molecules may be obtained by combining the results of experiments on the Kerr effect and on dipole moments. Finally Hund (Leipzig) was kind enough to illuminate all these questions from the point of view of modern quantum theory. He makes it quite plain that much work is still needed in this direction before it will be possible to calculate out the distribution of the charges, even for such a simple molecule as hydrogen chloride. But the way is now clearly marked out, and it is to be hoped that it will soon be traversed. Meanwhile the arguments which lead to the triangular structure for the water molecule and the pyramidal structure for the ammonia molecule, though necessarily rather mixed up with the older group of ideas, are not to be regarded with distrust.

Altogether I think I am justified in presenting this volume of papers to those who are interested in the subject. I am sure that the lectures which we in Leipzig had the privilege of hearing contain many valuable stimuli to further work.

In conclusion I wish to thank my assistant, Dr. Sack, for helping me in many ways in the organization of the conference and in seeing this book through the Press.

P. DEBYE.

LEIPZIG, 14th October, 1929.

PREFACE TO THE ENGLISH EDITION

In the preceding preface, translated from the German edition, a general outline has already been given of the different subjects treated in the lectures. It has not been necessary to change anything for the English translation. It is still true that the book contains the statement of many theoretical and experimental problems which are not yet solved. That is why it is a pleasure to me to see an English translation completed, in which the ideas of the different authors have been excellently reproduced.

P. DEBYE.

LEIPZIG, 23rd March, 1931.

CONTENTS

Page

NEW MEASUREMENTS ON THE EFFECT OF TEMPERATURE ON THE DIELECTRIC CONSTANTS OF GASES AND VAPOURS (R. Sänger, Zürich) - - 1

THE APPLICATION OF THE MOLECULAR-BEAM METHOD TO THE INVESTIGATION OF THE POLARITY OF MOLECULES (I. Estermann, Hamburg) 15

CHANGES IN THE POLARIZATION OF POLAR SUBSTANCES WITH CONCENTRATION AND TEMPERATURE (J. Errera, Brussels) - - - - - - 23

THE DIPOLE MOMENT AND MOLECULAR STRUCTURE (I. Estermann, Hamburg) - - - - - - 27

DIPOLE MOMENTS AND MOLECULAR CONSTITUTION (J. Errera and M. L. Sherrill, Brussels) - - - - 39

THE DIPOLE MOMENT AND INTRAMOLECULAR MOTIONS IN LARGE MOLECULES, ESPECIALLY IN THOSE OF ALIPHATIC COMPOUNDS (L. Ebert, Würzburg) - - - - - - - - - 43

SOME THEORETICAL REMARKS ON THE QUESTION OF THE ELECTRIC MOMENT AND THE CONFIGURATION OF MOLECULES (F. Hund, Leipzig) - 73

THE DIPOLE MOMENT AND THE VELOCITY OF REACTION (W. Hückel, Freiburg im Breisgau) - - - 79

THE ABSORPTION SPECTRA OF DI-SUBSTITUTED BENZENE COMPOUNDS (K. L. Wolf, Karlsruhe) - - 95

Page
MOLECULAR ASSOCIATIONS (J. Errera, Brussels) - - 101

A SIMPLE RELATIONSHIP BETWEEN THE REFRACTIVE INDEX AND DIELECTRIC CONSTANT OF REGULAR CRYSTALS AND THE COEFFICIENT OF REPULSION IN BORN AND LANDÉ'S POTENTIAL EQUATION (K. Højendahl, Copenhagen) - - 109

THE ATOMIC POLARIZATION (J. Errera, Brussels) - - 115

THE KERR EFFECT AND MOLECULAR STRUCTURE (K. L. Wolf, Karlsruhe) - - - - - - - 119

AUTHOR INDEX - - - - - - - - 129

SUBJECT INDEX - - - - - - - - 131

PLATE

PLATE ILLUSTRATING ESTERMANN'S PAPER - - - Facing p 20

THE DIPOLE MOMENT AND CHEMICAL STRUCTURE

New Measurements on the Effect of Temperature on the Dielectric Constants of Gases and Vapours.

R. SÄNGER, Zürich

I. Introduction

At the time when P. Debye * originated the dipole theory in order to explain the peculiar temperature variations in the dielectric constants of certain substances, most measurements of the alterations in dielectric constants with temperature had been made on liquids. The main point was that the theory should reproduce the behaviour of these liquids, but the agreement with actual measurements was anything but satisfactory. We now know that owing to our ignorance of the constant of the internal field the theory in the strict sense is only capable of explaining the effect of temperature on the dielectric constants of gases and vapours.†

The very first satisfactory experiments on gases ‡ gave good agreement with theory, although they had been carried out by an old method (in 1919 valves were not yet in general use). Once the valve technique had made accurate observation of the dielectric constants of gases possible and attention had been drawn to the problem by Debye's article in the *Handbuch der Radiologie*, Vol. VI, a number of papers on the effect of temperature on dielectric constants appeared within a short time. All the observers confirmed

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* P. Debye, *Phys. Zeitschr.*, **13**, 97 (1912).

† R. Sänger, *Phys. Zeitschr.*, **27**, 165 (1926).

‡ M. Jona, *Phys. Zeitschr.*, **20**, 19 (1919).

Debye's theory on the whole; in particular, the papers by Zahn *, Watson †, and Stuart ‡ may be mentioned. The measurements were carried out for various temperatures; the pressures and densities of the gas were chosen at random, i.e. were quite independent of each other. The electric moment μ was calculated from Debye's law

$$\frac{\epsilon - 1}{3} = \frac{4\pi}{3} n \left(a + \frac{\mu^2}{3k} \cdot \frac{1}{T} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where ϵ is the dielectric constant, n the number of molecules per c.c., a the polarizability of the molecule, μ the dipole moment, and k Boltzmann's constant) which may also be written in the form

$$P = \frac{\epsilon - 1}{3} \frac{M}{\rho} = \frac{4\pi}{3} N \left(a + \frac{\mu^2}{3k} \cdot \frac{1}{T} \right) = a + b \cdot \frac{1}{T} \quad . \quad (2)$$

(where M is the molecular weight, ρ the density, and N Avogadro's number). Within the limits of experimental error all the experiments confirm the linear relationship between the molecular polarization P and the temperature.

It is more in accordance with the spirit of the theory, however, to carry out measurements on the effect of temperature on dielectric constants not for a few arbitrary densities but with the density kept constant, i.e. with a constant number of molecules. Experiments fulfilling this condition not only exhibit the workings of Debye's law in a very beautiful way but will immediately reveal any effects of an associative nature which may be expected to occur when the density is large.

Some years ago, at Professor Debye's suggestion, I set up in the Zürich laboratory an apparatus by means of which the temperature variation of dielectric constants can be measured for a constant number of molecules.§ Various defects in the apparatus, in particular the use of ordinary brass condensers, prevented the dielectric constants being determined with the accuracy necessary for an accurate calculation of the electric moment, so that the moments could only be determined to about $0{\cdot}1 \cdot 10^{-18}$ e.s.u.

More recently O. Steiger and I constructed considerably improved apparatus, by means of which much more accurate determinations of dielectric constants may be made, and which therefore makes it possible to investigate the effect of temperature on the dielectric constants of gases and vapours systematically. We may state in anticipation that with the low densities used all the measurements confirm the linearity of the relationship between the dielectric constant and the reciprocal of the temperature which is required by Debye's law.

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* C. T. Zahn, *Phys. Rev.*, **24**, 400 (1924).

† H. E. Watson, *Proc. Roy. Soc.*, A, **117**, 43 (1927).

‡ H. A. Stuart, *Zeitschr. f. Physik*, **47**, 457 (1928).

§ R. Sänger, *Phys. Zeitschr.*, **27**, 566 (1926).

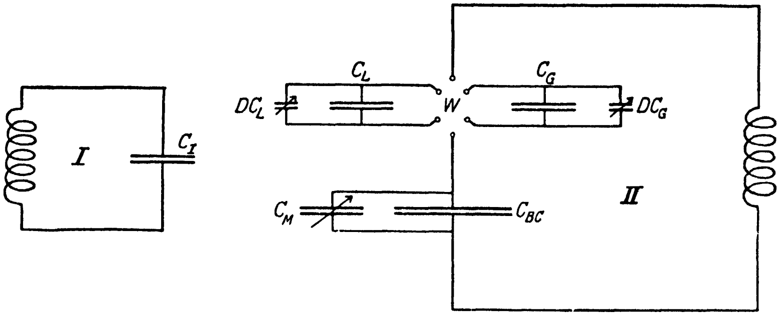

Fig. 1

The apparatus and method of experiment are fully described in our paper on water vapour (R. Sänger and O. Steiger, *Helvetica Phys. Acta*, Vol. I, p. 369 (1928)). Here we shall merely discuss some of the more important points.

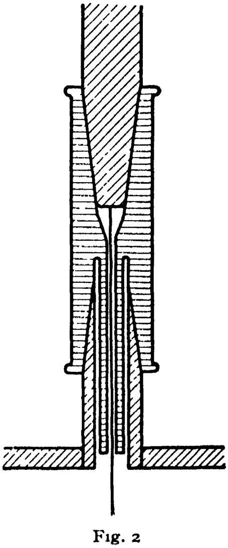

Fig. 2

A heterodyne method first suggested by Preuner and Pungs[*] was used to determine the dielectric constants. The apparatus is shown diagrammatically in fig. 1.

Two Radio-Corporation amplifiers (CX 371 A) with a filament temperature of about 800° C. are used as a source of current. Variations of temperature have very little effect on the frequency. The gas-filled condenser C_G is compared with a condenser C_L (filled with nitrogen) of exactly the same construction. Each condenser consists of nine heavily gilt precision cylinders with a total capacity of 2070 cm. The gas and air condensers are fitted into a metal boiler in a bath of about 50 litres of paraffin oil. The range of temperature of the bath is from room temperature to about 300° C. A quartz compensation manometer connected with the boiler by an invar-quartz joint enables the pressure of the gas to be measured correct to 1/10 mm. One side of the condenser is connected to the boiler direct; electrical connexion with

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[*] G. Preuner and L. Pungs, *Phys. Zeitschr.*, **20**, 543 (1919).

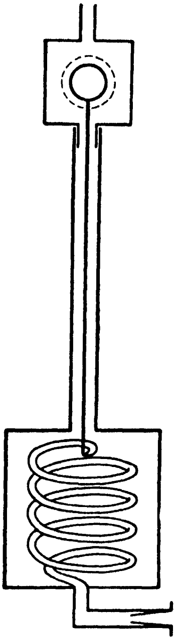

Fig. 3

the other side is made by means of a double quartz-invar joint. Figs. 2 and 3 show the manometer and double joint.

C_M in fig. 1 denotes a Seibt standard condenser with a maximum capacity of 2000 cm. and a fine scale of 8000 divisions. A block condenser of capacity about 18,000 cm. is connected in parallel with it and in series with the gas or air condenser. The apparatus enables the standard condenser to be adjusted accurately to one or two scale divisions. The sensitivity is such that $\varepsilon - 1$ may be determined accurately to 1 per cent.

II. The Equation of State

In order to measure the effect of temperature on dielectric constants at constant density, we have first to determine the equation of state of the gases and vapours under investigation. This is done as follows: the vapour being investigated is led into the gas-holder at a density which in the first instance is selected arbitrarily, and the quartz manometer then enables us to find the pressure at various temperatures when the density is kept at this constant value.

According to van der Waals' equation the relationship between pressure and temperature is

$$p = -\frac{a}{v^2} + \frac{RT}{v - b}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or for a constant gram-molecular volume v

$$p = -C + DT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

The fairly numerous results already obtained by various workers exhibit marked deviations from van der Waals' equation. Hence we may not assume without further investigation that the variation of the pressure with temperature follows the linear law required by equation (3′). In reality, however, the measurements described in what follows show that when the density is taken sufficiently small the pressure does obey a linear law within the limits of experimental error; but the constants C and D which determine the relationship between pressure and temperature may differ considerably from the values deduced from the critical data.

If deviations from the linear law occur when the density is

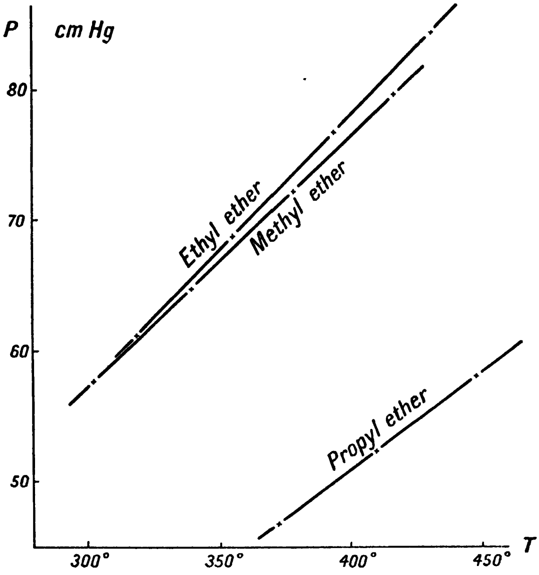

Fig. 4

greater, we must ascribe them chiefly to associative influences. Thus if the linear law required by (3′) is confirmed by experiment when the density is sufficiently small we may with fair security expect

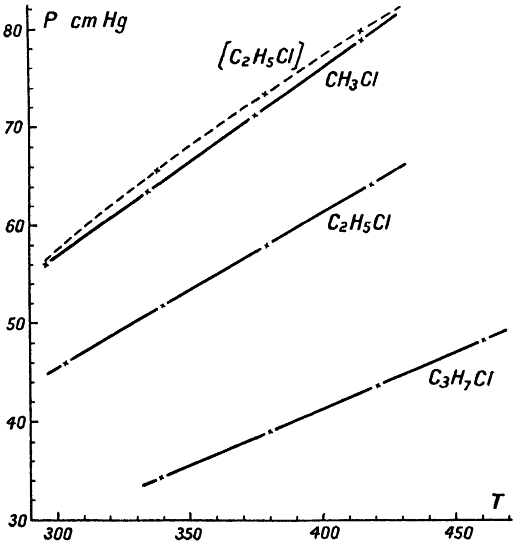

Fig. 5

that association will have no important effects on the behaviour of the dielectric constants either, so that the dielectric constants will obey Debye's law strictly. If, then, deviations from the linear law required by (3′) should occur in any experiment, we should have to pass to a density smaller than that with which we had selected to work.

Figs. 4 and 5 show the relationship between temperature and pressure found by experiment in the case of the vapours of methyl, ethyl, and propyl ether and methyl, ethyl, and propyl chloride. As the temperature variation of the pressure of aqueous vapour is already sufficiently well known, it is unnecessary to make special measurements of it on this occasion.

The graphs shown in the figures are for the following constant densities:

Methyl ether $\rho = 0{\cdot}00137$ gm./c.c.
Ethyl ether $\rho = 0{\cdot}00237$ gm./c.c.
Propyl ether $\rho = 0{\cdot}00213$ gm./c.c.
Methyl chloride $\rho = 0{\cdot}00156$ gm./c.c.
Ethyl chloride $(\rho = 0{\cdot}00200$ gm./c.c.)
$\rho = 0{\cdot}00160$ gm./c.c.
Propyl chloride $\rho = 0{\cdot}00133$ gm./c.c.

The densities of methyl ether and ethyl ether were calculated from Stuart's determinations of absolute density.* The corrections involved were small, so that the above values are sufficiently accurate for our purposes. No satisfactory figures are available for the other substances, so that the densities given were merely calculated by applying the gas laws to the experimental conditions for the highest temperature used in the experiment. These, therefore, can only claim to be approximate values; the errors, however, are relatively trifling, and no larger errors will enter into the subsequent calculation of the electric moment.†

The relationship between pressure and temperature in the case of ethyl chloride is given for two different constant densities in fig. 5. As is clearly shown by the figure, the pressure does not increase linearly for the larger of the two densities selected (that given in brackets) but does so for the slightly smaller value of the density.

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* H. A. Stuart, *Zeitschr. f. Physik*, **51**, 490 (1928).

† For further vapour pressure measurements made at various temperatures and pressures by means of specially designed apparatus, see O. Steiger, *Dissertation* (Eidgenössische Technische Hochschule, Zürich).

In view of this the measurement of the dielectric constant was carried out for the smaller density only.

In spite of the fairly high densities used for the experiments on ethyl ether and propyl ether (at the lowest temperature used in the experiment the vapour pressure of ethyl ether is nearly equal to the saturation pressure), the pressure is found to obey a purely linear law. This difference of behaviour between the ethers and the chlorides is in complete agreement with K. L. Wolf's recent deductions from the dielectric properties of mixtures of liquids.* In his paper Wolf attempts to explain the occurrence of association as being chiefly due to the presence of dipoles. If, as in the case of the ethers, the definitely polar parts of the molecule are sheltered by neutral alkyl groups on either side—and in this his statements are in complete agreement with our results—association phenomena will only occur to a trifling extent, whereas if the alkyl groups are terminal, as in the chlorides, marked association phenomena must occur.

III. Measurement of the Dielectric Constants

The measurement of the dielectric constants of the various vapours was carried out under the conditions described in the previous section, i.e. at the vapour pressures found to correspond to the various temperatures. In this way we obtain the effect of temperature on the dielectric constants when the density has a constant known value. In the following tables the absolute temperature is given in the first column and its reciprocal in the second. The third column gives the pressure calculated from the equation of state and used in the measurement of the dielectric constants. Finally, the last column gives the measured values of the dielectric constants. The results obtained are illustrated graphically in figs. 6, 7 and 8.

TABLE I

WATER

T	$10^3/T$	p	$(\epsilon - 1) \times 10^5$
393·0	2·545	56·49	400·2
423·0	2·364	60·93	371·7
453·0	2·207	65·34	348·8
483·0	2·070	69·75	328·7

$$\mu = (1{\cdot}84_7 \pm 0{\cdot}02)10^{-18}.$$

---

* K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, 2, 39 (1929).

All the results confirm the fact (required by Debye's law) that the dielectric constant is a linear function of the reciprocal of the temperature. The electric moments (μ) of the molecules calculated from the slopes of the lines are in each case given under the table.

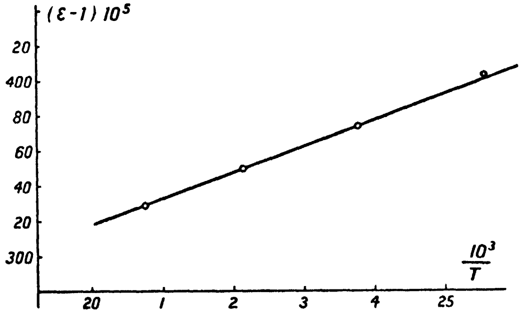

Fig. 6

As the figure shows, the point corresponding to a temperature of 120° C. is a little off the straight line drawn through the three other points. Presumably this deviation is to be ascribed to association, or perhaps to adsorption. Only the three upper points have been used in the evaluation of the electric moment.

TABLE II

ETHERS

T	$10^3/T$	p	$(\varepsilon-1)\times 10^5$
	Methyl ether		
298·0	3·356	57·00	465·5
338·0	2·959	64·86	426·7
378·0	2·646	72·68	398·1
418·0	2·392	80·56	372·2
	Ethyl ether		
313·0	3·195	60·26	495·0
353·0	2·833	68·67	470·0
393·0	2·545	77·02	450·7
433·0	2·310	85·26	431·0
	Propyl ether		
368·0	2·717	46·28	359·7
408·0	2·451	52·26	353·2
448·0	2·232	58·24	346·2

μ for methyl ether $(1{\cdot}32 \pm 0{\cdot}02)10^{-18}$, for ethyl ether $(1{\cdot}10 \pm 0{\cdot}02)10^{-18}$, for propyl ether $(0{\cdot}85 \pm 0{\cdot}03)10^{-18}$.

Owing to the somewhat greater uncertainty as regards the density and the small range of temperature available the range of possible error in the electric moment is somewhat larger for propyl ether than for the two other ethers. Fig. 7 represents the temperature variation, not of the dielectric constants, but of the molecular polarizations; in the case of constant density this merely involves multiplication by a constant factor.

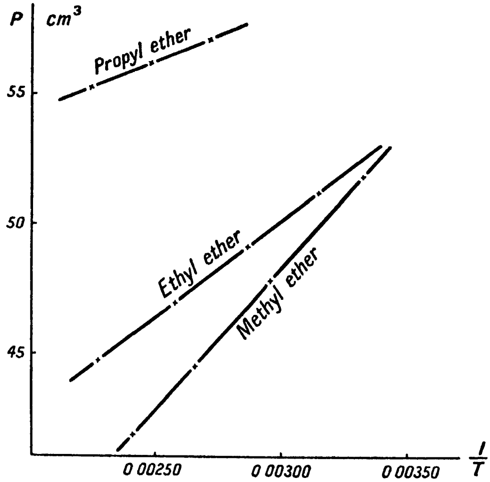

Fig. 7

TABLE III

Chlorides

T	$10^3/T$	p	$(\epsilon - 1) \times 10^5$
	Methyl chloride		
298·0	3·356	56·84	797·6
338·0	2·959	64·67	718·3
378·0	2·646	72·60	657·8
418·0	2·392	80·58	607·2
	Ethyl chloride		
298·0	3·356	45·47	773·0
338·0	2·959	52·14	702·6
378·0	2·646	58·65	642·6
418·0	2·392	64·75	599·4

μ for methyl chloride $(1{\cdot}86 \pm 0{\cdot}03)10^{-18}$,
for ethyl chloride $(1{\cdot}99 \pm 0{\cdot}03)10^{-18}$.

The relatively large possible errors are due to uncertainty as to the density. When it becomes possible to measure the density accurately it will be possible to give more accurate values for the electric moments of the chlorides. No results for propyl chloride are given in Table III, as the experiments are not yet complete.

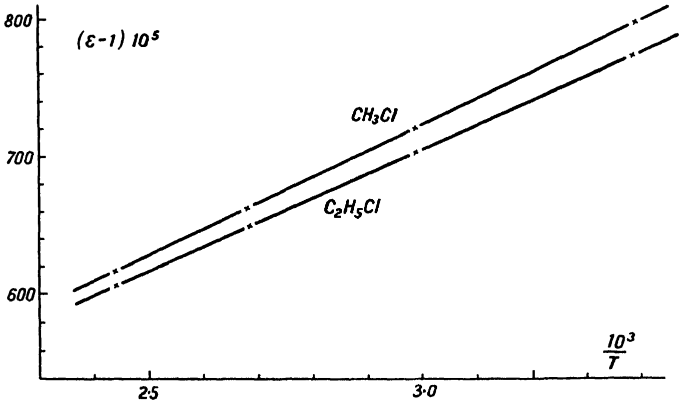

Fig. 8

IV. Discussion of the Electric Moments

The fact that an electric moment exists in the case of the water molecule indicates that it has a triangular structure with the O-ion at the vertex. As a matter of fact Hund * has also shown from energy considerations that the water molecule cannot be represented except by an angular model. From the infra-red absorption bands we obtain two solutions for the water molecule, one with a vertical angle θ of 64°, the other with $\theta = 110°$. Both solutions give almost the same value for the distance of the O-ion from the two H-ions ($a = 1{\cdot}0 \times 10^{-8}$ cm.). If by introducing the polarizability of the O-ion we calculate the electric moments corresponding to the two models, we obtain the values † $\mu = 1{\cdot}34 \times 10^{-18}$ and $\mu = 4{\cdot}32 \times 10^{-18}$. Comparison with the experimental value is at first glance rather in favour of the acute-angled model; but, as Herr Hund emphasized in the discussion, we may take it that either theoretical value is consistent with the experimental value.

The electric moments found for the ethers are likewise in favour

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* F. Hund, *Zeitschr. f. Physik*, **31**, 81 (1925); **32**, 1 (1925).

† P. Debye, *Polare Molekeln*, p. 80 (S. Hirzel, Leipzig); *Polar Molecules*, p. 68 (Chemical Catalog Co., New York).

of a triangular structure. The decrease in the moment with increasing molecular weight of the alkyl group would then mean that the vertical angle increases as we pass from methyl ether to ethyl ether and propyl ether. This statement is consistent with the results obtained for the two chlorides, where the rise in the molecular weight of the alkyl group leads to an increase in the electric moment.* Hence in the case of the ethers the decrease in the electric moment with increasing molecular weight of the alkyl group can only be explained by an increase in the vertical angle.

V. The Infra-red Term in the Dielectric Constants

In Debye's law for the molecular polarization

$$P = \frac{\epsilon - 1}{3} \frac{M}{\rho} = a + b \cdot \frac{1}{T},$$

a represents the optical polarization

$$P_o = a = \frac{4\pi}{3} N \cdot \alpha,$$

which should accordingly coincide with the molecular refraction

$$P_r = \frac{n^2 - 1}{3} \frac{M}{\rho}.$$

In this equation defining P_r, n denotes the refractive index extrapolated for infinite wave-length. This extrapolation is usually performed by means of a single ultra-violet absorption frequency. But as the infra-red dispersion is completely neglected in the above, we may expect discrepancies between P_o and P_r to occur and to be specially conspicuous in the case of polar molecules. We may suppose that the infra-red contribution $P_r - P_o$, together with the dipole moment, increases as the size of the molecule increases. These relationships are illustrated in a particularly beautiful way in the case of the ethers we investigated. For water the difference between P_0 and P_r obtained by experiment falls within the range of experimental error.

---

* Since the above was written the electric moment of propyl chloride has been found to have the value $\mu = (1{\cdot}87 \pm 0{\cdot}04)10^{-18}$. At first sight the decrease in the electric moment as we pass from ethyl chloride to propyl chloride is surprising. If we regard the chlorides as a sort of ionic compound like the hydrogen halides—in spite of the rather daring idea—an increase in the polarizability of the alkyl ion without any change in the distance between the ions would cause a decrease in the electric moment. But as increasing the alkyl group does not merely mean an increase in the polarizability, the result for the alkyl chlorides is to some extent understandable.

In the following table the values of P_r and P_0 are given in the second and third columns respectively.

TABLE IV

Substance	P_r	P_0
Methyl ether ..	13·68 c.c.	15·97 c.c.
Ethyl ether ..	24·18 ,,	27·84 ,,
Propyl ether ..	31·71 ,,	45·53 ,,
Methyl chloride ..	11·7 ,,	14·6 ,,
Ethyl chloride ..	19·2 ,,	22·2 ,,

The extrapolation to wave-length ∞ was carried out for ethyl ether only. In the case of methyl ether the refractive index is known only for a wave-length from which it is impossible to extrapolate. Extrapolation, however, only means a trifling alteration in n, so that it is of no importance here, where the differences between P_0 and P_r are large. As at the present time the densities of the chlorides and of propyl ether are not known with sufficient accuracy, it is clearly useless to carry out the extrapolation. In the case of propyl ether no values for n in the gaseous state are available; the value of the molecular refraction given in the table above was calculated from a value of n for the liquid state, assuming the validity of the Lorentz-Lorenz equation. Perhaps this is the reason why the value of P_r for propyl ether seems rather too small compared with the values for the other ethers.

Although the values in Table IV, other than those for ethyl ether and methyl ether, require small corrections, the table shows without any doubt that a difference between P_r and P_0 does exist. This difference, which we may regard as the infra-red contribution to the dielectric constant, increases with increasing molecular weight of the alkyl group in the case of the ethers, i.e. it appears to depend essentially on the size of the molecule; in general it will also be affected by the magnitude of the dipole moment. The infra-red terms for the chlorides cannot of course be compared until the densities are known accurately. The results available so far do not permit of any thorough discussion.

The existence of the infra-red contribution to the dielectric constant also explains why measurements of the molecular polarization of mixtures of liquids at a single temperature do not yield accurate values of the electric moments, inasmuch as the infra-red part cannot then be evaluated in any way. Thus for example Williams obtained the value $\mu = 1{\cdot}22 \times 10^{18}$ for ethyl ether from his experiments on mixtures of liquids, whereas we got $\mu = 1{\cdot}10 \times 10^{-18}$. The difference of about 10 per cent between the values corresponds to the ratio of the difference $P_o - P_r$ to P_{total} (at about 350° C.), which comes to about 20 per cent in this case.

VI. Comparison with other Results

Two papers have recently been published on the effect of temperature on the dielectric constants of gases and vapours, in which among others some of the substances discussed above were studied. These measurements were not all made at constant density, but as the densities used were as a rule very small no important deviations are likely to occur.

In the first place we mention Stuart's experiments on methyl and ethyl ether.* The densities worked with were determined experimentally, and, as we mentioned above, exhibit large deviations from the densities as calculated from the gas laws (cf. the section on the Equation of State, p. 4).

As Stuart worked with very small densities which were determined experimentally, and in addition the values of the molecular polarization calculated from the measured values of the dielectric constants and the corresponding densities are strictly in accordance with Debye's law, the values of the electric moment obtained from the variation of the molecular polarization with temperature must be regarded as being very accurate. We should therefore expect that the results we obtained should agree with Stuart's within the range of experimental error, if the methods used are genuinely successful.

Stuart obtains $\mu = (1{\cdot}29 \pm 0{\cdot}03)10^{18}$ for methyl ether and $\mu = (1{\cdot}14 \pm 0{\cdot}03)\,10^{18}$ for ethyl ether; our values are $\mu = (1{\cdot}32 \pm 0\,02)10^{18}$ for methyl ether and $\mu = (1{\cdot}10 \pm 0\,02)10^{18}$ for ethyl ether. The complete agreement within the limits of possible error means that not only are the values found for the electric moment of the two substances accurate, but the relatively large deviations from the values determined for mixtures of liquids do really exist. These differences caused by the infra-red contribution to the dielectric constants are also in the direction to be expected, the results derived from the mixtures of liquids being somewhat larger throughout. Really definite satisfactory values are only to be expected from measurements of the dielectric constants of gases and vapours.

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* H. A. Stuart, *Zeitschr. f. Physik*, **51**, 490 (1928).

The second paper to be referred to in this connexion is by Sircar,[*] and deals with measurements of the dielectric constants of methyl chloride and ethyl chloride. Sircar gives the following electric moments for the two substances:

$$\begin{aligned}&\text{Methyl chloride} \quad \mu = 1{\cdot}69 \times 10^{18},\\ &\text{Ethyl chloride} \quad \mu = 1{\cdot}98 \times 10^{-18}.\end{aligned}$$

While the electric moment of ethyl chloride—perhaps by chance—agrees very well with the value given in our table, the values for the electric moment of methyl chloride differ from each other by a considerable amount, at any rate by an amount exceeding the range of experimental error. Although Sircar's value for methyl chloride is in better agreement with the value deduced by Raman [†] from the Kerr effect, we may take it that Sircar's value is too small: for one thing, the individual measurements were made at widely differing densities (in contradistinction to those of Stuart); and besides this—perhaps the chief source of error lies here—the densities used at the various temperatures were simply calculated from the ordinary gas laws, the latter being introduced into Debye's equation for the molecular polarization by eliminating the density ρ.[‡]

[*] S. C. Sircar, *Indian Journal of Physics*, **3**, 197 (1928).

[†] C. V. Raman and K. S. Krishnan, *Phil. Mag.*, **3**, 714 (1927).

[‡] The values found for the electric moments of ethyl bromide and methyl iodide by P. C. Mahanti, *Indian Journal of Physics*, **3**, 181 (1928), using the same method, are likewise low in comparison with other results (see e.g. Smyth and Morgan, *Jour. Amer. Chem. Soc.*, **50**, 1547 (1928) for ethyl bromide, and Williams, *Zeitschr. f. phys. Chemie*, A, **138**, 75 (1928) for methyl iodide).

The Application of the Molecular-Beam Method to the Investigation of the Polarity of Molecules.

I. ESTERMANN, Hamburg

Among all the methods which have hitherto been brought forward for the determination of the electric dipole moment of molecules, the molecular-beam method occupies a special position, for it enables us to investigate the behaviour of individual free molecules in the electric field directly. It also has the great advantage that the effect of the field on the dipole moment of a single molecule occurs in it as a directly measurable quantity, so that it avoids the uncertainties of all other methods, which are chiefly due to the fact that in their case it is the macroscopic actions between the field and the dielectric (gas or liquid) which are measured and the mutual effects of the molecules can neither be eliminated entirely nor be allowed for accurately.

The molecular-beam method has the further advantage that it can be used in many cases where the other methods cannot be applied. The methods in general use for the determination of dipole moments depend on the measurement of the dielectric constant of the substance in question in the form of vapour or of a dilute solution in a non-polar solvent, usually benzene. Many of the substances which do not dissolve to a sufficient extent in a solvent of this type and which cannot be transformed into vapour with a pressure suitable for the measurement of the dielectric constant can be investigated by means of the molecular-beam method, as the latter merely requires that it should be possible to sublimate the substance in a high vacuum.

The principle of the molecular-beam method consists in letting a " molecular beam " be affected by external conditions. A molecular beam is produced by making a gas or vapour enter a highly-evacuated space through a small slit. A second slit is used to select, from among the swarm of molecules spreading out in straight lines in all directions with their thermal velocities, those particular molecules which are moving along the line joining the two slits. The molecular-beam method has already been much used in the study of atomic problems, especially in investigations of the magnetic moments of atoms. Its applicability to the determination of electric dipole moments was first discussed by Kallmann and Reiche * and later by Stern.† This depends on the fact that a molecule carrying an electric dipole in a non-uniform electric field is acted on by a ponderomotive force, so that a beam of such molecules traversing a non-uniform field suffers deviation. The magnitude of the deviation depends, apart from the conditions of experiment (the strength and degree of non-uniformity of the electric field and the dimensions of the beam), on the magnitude of the dipole moment, the velocity of the molecules, and the angle between the direction of the field and the direction of the dipole. In the analogous magnetic case, so far as investigations have been carried out hitherto, the molecules involved have been monatomic; owing to the quantum conditions (azimuthal quantization) these can only set themselves at a few definite angles to the direction of the field. Hence a beam of such atoms is split up into several distinct beams. If, however, we were dealing with polyatomic polar molecules the dipole moment would in the first instance vanish owing to the thermal rotations of the molecules, and a moment proportional to the intensity of the field would only arise as a result of the influence of the field on the rotation. The magnitude of this induced moment also depends on the velocity of rotation, which according to the quantum theory further determines the directions of the molecular axis in the field. As the rotational quantum numbers are very large when the moments of inertia are large and the temperatures moderate or high (as has hitherto been the case), practically any velocity of rotation or any position in the field is possible. Thus we obtain no distinct splitting-up, but as attractions and repulsions take place there is merely a spreading of the beam on either side, the extent of which may be calculated from classical theorems. The calculations are very complicated and will not be reproduced here; in order that we should be able to determine the dipole moments from experiments of this kind it would be necessary to know the distribution of intensity in the deflected beam. In the experiments hitherto carried out, of course, it has been impossible to measure the

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* H. Kallmann and F. Reiche, *Zeitschr. f. Physik*, **6**, 352 (1921).

† O. Stern, *Phys. Zeitschr.*, **23**, 476 (1922); *Zeitschr. f. Physik*, **39**, 761 (1926).

intensity distribution accurately, so that the electric moments could not be determined quantitatively in this way. There is no doubt, however, that it is possible to settle the question of the existence of an electric moment conclusively and to estimate its order of magnitude. By working under very constant conditions (with the same intensity and degree of non-uniformity of the electric field, the same size of beam, and as nearly as possible the same molecular velocities) the broadening of the beam may be taken as measuring the dipole moment directly, so that the moments of molecules which chemically are very similar to each other (e.g. isomeric compounds) may be compared by this method.

In discussing the experiments we must bear in mind that owing to the polarizability of molecules even a non-polar molecule acquires a moment in the electric field. This induced moment, however, is always parallel to the direction of the field, independently of the position and rotation of the molecule, so that the molecule is always attracted. Hence even in the case of non-polar substances we may expect to find the molecular beam deflected to one side, in the direction in which the field varies. When polar substances are used this unilateral deviation is superposed on the broadening due to the natural dipoles.

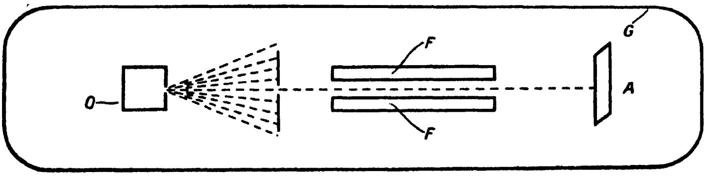

Fig. 1

The arrangement of the experiment is shown diagrammatically in fig. 1. A furnace O in a highly-evacuated vessel G is used to vaporize the substance. The molecules stream from the furnace slit in straight lines in all directions. A beam is selected from this cone of molecules by the image-forming slit; this beam traverses the electric field FF and is stopped by the collector A. The first experiments of this kind were carried out by Wrede * on the binary salts KI, TlI, NaI, CsCl, and RbBr. The methods of experiment were developed further by the author † and specially adapted to the investigation of readily vaporizable organic substances. Fig. 2

* E. Wrede, *Zeitschr. f. Physik*, **44**, 261 (1927).

† I. Estermann, *Zeitschr. f. phys. Chemie*, B, **1**, 161 (1928).

is a sketch of his apparatus; the internal part (" metal apparatus ") is shown in greater detail in fig. 3. The beams again start from the furnace slit (1). A narrow beam is isolated by means of the image-forming slit (3), which is rigidly connected to the furnace by two strips of constantan. The narrow beam then traverses a non-uniform electric field, produced in the condenser (4), which consists of a knife-edge and half-cylinder; the beam finally impinges on the collector (5), which is cooled with liquid air. The resulting image is observed from outside by a microscope with the help of the prism (6) through the window (7). The furnace is constructed in such a way that the furnace slit has the highest temperature. The thermo-couple (13) for measuring the temperature of the furnace is attached at the end of the box (11) which holds the substance under investigation, so that it measures the lowest temperature determining the vapour pressure. The image-forming slit is in a block of phosphor bronze, to which the constantan strips supporting the furnace are hard-soldered, and (15), the support of

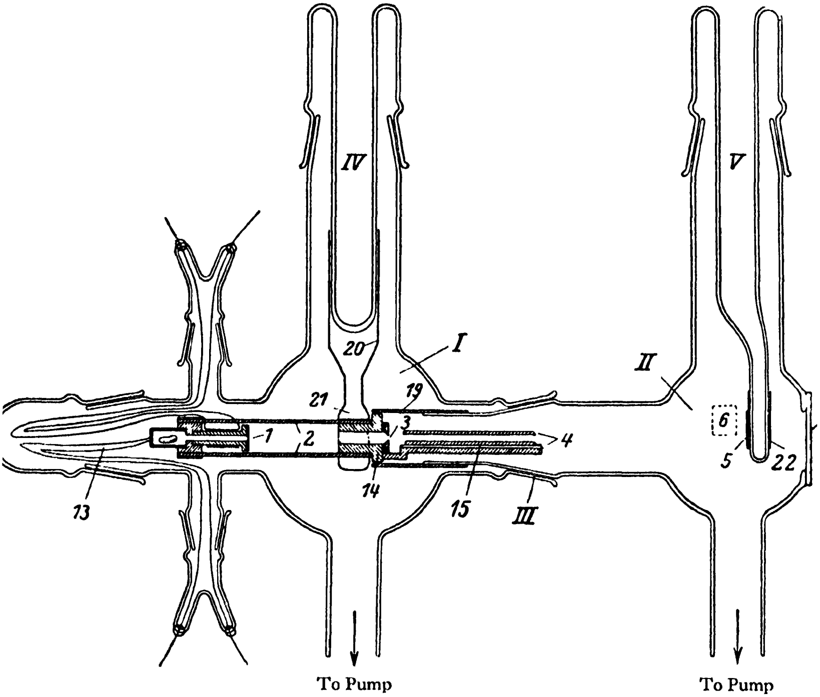

Fig. 2.—(From *Zeitschr. f. phys. Chemie*, B, **1**, 161 (1928))

the knife-edge of the condenser, is screwed. The knife-edge (16), a triangular brass rod with a wire of radius 0·5 mm. embedded in it, is adjustably fixed to the support by two clamps and two screws. The half-cylinder (17) which forms the outer coating of the condenser is insulated from the support by two u-shaped glass rods. The whole of the metal apparatus is enclosed in the " glass apparatus ", which consists of two parts. The furnace space (I) and the field space (II) are connected at the joint (III). A brass casing, to which the metal apparatus is screwed, is fixed to the prolongation of the inner member of the joint. Thus the furnace space and the field space are completely separated from each other except where they communicate by the image-forming slit. Stray radiation from the furnace is thereby prevented from reaching the field space and impairing the vacuum in it. The metal apparatus is cooled with liquid air by means of a casing (21) with spring clips fixed to the Dewar flask (IV). The collector-vessel (V) carries a brass collar (22) to which is fixed the collector, which consists of a polished plate of nickel. The furnace space and the field space are evacuated by two separate diffusion pumps.

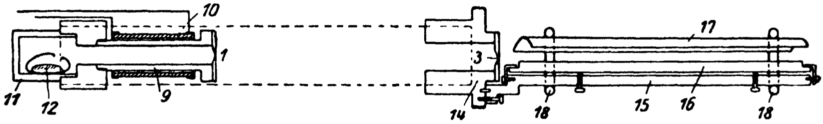

Fig. 3.—(From *Zeitschr. f. phys. Chemie*, B, **1**, 161 (1928))

The experimental data and the dimensions of the apparatus were as follows: furnace slit 1 × 0·01 mm., image-forming slit 2 × 0·02 mm., distance between furnace slit and image-forming slit 6 cm., length of condenser 6 cm., total length of beam 20 cm. The radius of curvature of the knife-edge was 0·5 mm., that of the half-cylinder 2·5 mm., and the distance of the centre of the beam from the knife-edge 0·3 mm. The applied pressure, which was produced by a small induction machine, was 21,000 volts (70 electrostatic units). For the calculation of the intensity of the field the apparatus is regarded as a cylindrical condenser; we then obtain $E = 1{\cdot}63 \times 10^5$ volts/cm. for the intensity of the field at the place occupied by the beam, and $dE/dr = 2 \times 10^6$ volts/sq. cm. for the rate of variation of the field. The furnace temperature lay between 100° and 200° C.

In order to test the apparatus the first substances investigated were those for which the electric moment was already known from measurements of the dielectric constants in dilute solution. The results are shown in Table I.

TABLE I

Substance.	Lateral Displacement in mm.	Maximum Breadth in mm.	Moment by Dielectric-constant Method.
Diphenyl	about 0·1	$< 0·15$	0
Diphenylmethane	„ 0·1	$< 0·15$	$< 0·4 \times 10^{-18}$
Phenyl ether	„ 0·1	about 0·30	$1·0 \times 10^{-18}$
Benzophenone	„ 0·15	„ 0·60	$2·5 \times 10^{-18}$
Methyl ester of *o*-aminobenzoic acid	„ 0·1	„ 0·25	$1·0 \times 10^{-18}$
Methyl ester of *m*-aminobenzoic acid	„ 0·1	„ 0·5	$2·4 \times 10^{-18}$
Methyl ester of *p*-aminobenzoic acid	„ 0·1	„ 0·7	$3·3 \times 10^{-18}$

According to these experiments, then, diphenyl and diphenylmethane have no appreciable electric moment; this agrees with the results of other investigations. In the case of the other substances satisfactory values for the moments are obtained, and if they are arranged in order according to the breadth of the deviated bands, the order is the same as that obtained from measurements of the dielectric constants. The approximate calculation of the moments from the breadth of the deviated bands leads to the order of magnitude 10^{-18} c.g.s. units, i.e. agrees with the results obtained by other means.

These results having been obtained, the method was used to investigate a problem of fundamental importance in the realm of chemical constitution. According to Weissenberg's theory,* substances of the type $C\alpha_4$, i.e. methane derivatives with all four substituents the same, should not only be able to exist in the form of a regular tetrahedron, but there should also exist molecular forms in which the C-atom is situated at the vertex of a pyramid and the four substituents at the four corners of the base. Molecules with the first type of structure should have no electric moment, whereas those with the second type should exhibit a permanent dipole moment. Pentaerythritol, $C(CH_2OH)_4$, is frequently quoted as an example of the second type of structure. The moment of this substance cannot be found by the dielectric-constant method, as it

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* I. Estermann, *Zeitschr. f. phys. Chemie*, 2, 287 (1929).

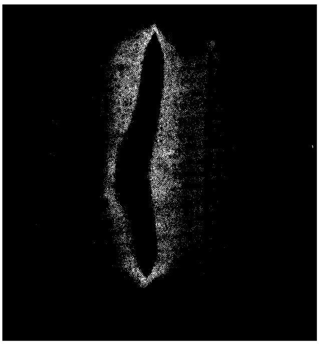

Fig. 4.—Pentaerythritol

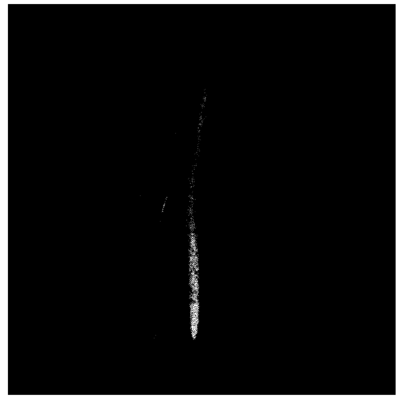

Fig. 5.—Pentaerythritol tetrabromide

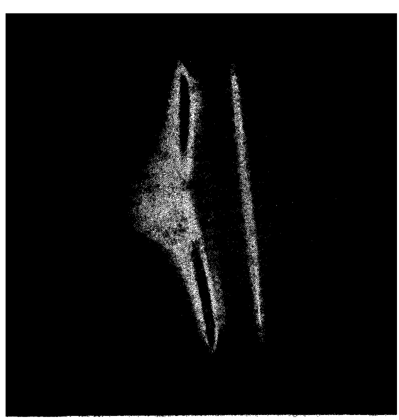

Fig. 6.—Pentaerythritol tetra-acetate

is insoluble in dielectrically neutral solvents and cannot be transformed into sufficiently dense vapour. The molecular-beam method clearly indicates the presence of a permanent dipole moment in the pentaerythritol molecule.* From the deviation obtained—a streak obtained with the field off is shown in the right-hand side of fig. 4, and one with the field on on the left—we find, using the results given in Table I, that the moment is about $2 \cdot 10^{-18}$ c.g.s. units. Some other substances of the type $C\alpha_4$ (derivatives of pentaerythritol), for which the moment had already been determined by the dielectric-constant method, were subsequently investigated by Estermann and Wohlwill.† The tetrabromide (fig. 5) shows no moment, which is in agreement with the dielectric-constant measurements; we merely see a trifling lateral displacement of the streak at the place of greatest variation of the field, due to the polarizability of the molecules. On the other hand, the tetra-acetate exhibits a very marked broadening, which indicates the existence of a fairly large moment, as has also been shown by the experiments of Ebert and his co-workers just mentioned.‡ Here we shall leave open the question whether Weissenberg's theory is really confirmed by the fact that there exist molecules of the type $C\alpha_4$ with a dipole moment, i.e. whether the central carbon atom exhibits *pyramidal* symmetry in these molecules. We should merely like to draw the conclusion from our results that *as a whole* the pentaerythritol molecule exhibits no central (tetrahedral) symmetry. The various possible ways of explaining the dipole moment of such compounds are discussed in Ebert's paper in this book (p. 43).

Molecular beam experiments on electric dipole moments are being prosecuted further in two directions. On the one hand, other substances in which the usual methods are inapplicable, but where a knowledge of the dipole moment is of interest from the viewpoint of structural chemistry, are being studied, and on the other hand, attempts are being made to work out a method which will enable us to measure the intensity distribution in the deflected beam and thus attain the real goal, namely the quantitative measurement of dipole moments by this method.

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* I. Estermann, *Zeitschr. f. phys. Chemie*, **2**, 287 (1929).

† Results as yet unpublished.

‡ L. Ebert, R. Eisenschitz, and H. von Hartel, *Zeitschr. f. phys. Chemie*, B, **1**, 94 (1928).

Changes in the Polarization of Polar Substances with Concentration and Temperature.

J. ERRERA, BRUSSELS

As I mention in another paper (p. 101), two outstanding types of polarization curve are obtained for polar substances dissolved in non-polar solvents. In the first type of curve P_2 always diminishes as C_2 increases. The second type is less simple; it exhibits a maximum for P_2, usually when the concentration is low (such curves are chiefly exhibited by the lower alcohols): see figs. 1 and 2, p. 104. For the explanation we refer the reader to Debye's article in the *Handbuch der Radiologie*. More complicated P_2-curves, e.g. those with several maxima, will not be discussed here.

We shall now investigate more closely how a curve of the second type changes with change of temperature.

Three regions of the curve may be distinguished: that of very low concentration (C_2 less than 0·1), that of the maximum, and that giving the polarization of the pure body.

It is known that the maximum of the P_2-curve has nothing to do with any maximum which may occur in the curve of total polarization.

Stranathan * has made quite a number of measurements on alcohols in the region of great dilution (see figs. 1 and 2). It will be noticed that the P_2-curves for one and the same substance (methyl alcohol) are quite different for different non-polar solvents: in one case P_2 is greater the higher the temperature and in another greater the lower the temperature. The terminal values also differ. At 10° C. $P_2 = 67$ in benzene solution and 53 in CCl_4. We have found that the same occurs with solutions of ethyl alcohol. With benzene as solvent we obtain the same curves as Stranathan, and at 20° C. P_2 has the value 72. When the methyl alcohol is mixed with hexane we find that the P_2-curves run the other way; P_2 has a maximum at a low temperature. The value of P_2 is also different (48).

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* *Phys. Rev.*, **31**, 653 (1928).

The change in the maximum region with temperature had already been studied by Lange.* We have also made measurements on this region in the case of a mixture of ethyl alcohol and hexane. Fig. 3 shows our results for this case; the first region and also the last region for the pure substance (plotted from Isnardi's results †) are clearly seen. We observe that the maximum value increases as the temperature diminishes. The reverse is true for P_2 in the pure state: P_2 decreases with the temperature.

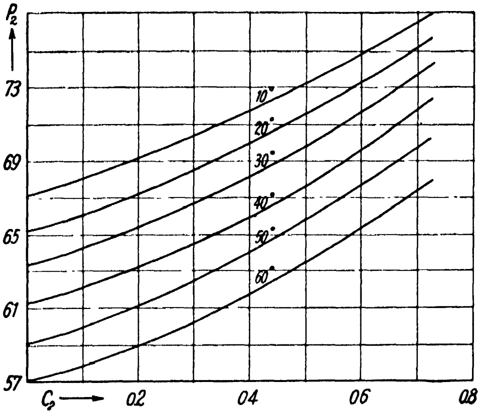

Fig. 1.—Methyl Alcohol in Benzene (Stranathan)

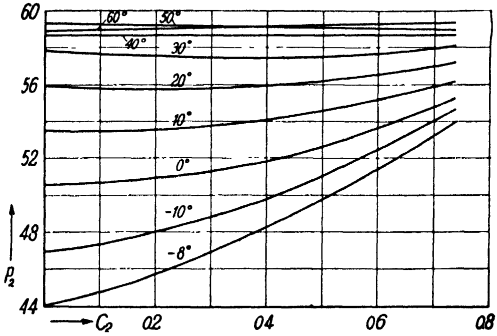

Fig. 2.—Methyl Alcohol in CCl_4 (Stranathan)

As the reader will see, the phenomena are quite complicated and not readily intelligible. We proceed to consider what would be required to transform these curves of the second type into curves of the first type. An increase of only a few per cent in the dielectric constant would suffice (the reader should remember that a difference of 1 per cent in the dielectric constant may involve a difference of ten units in the value of P_2 for this range of concentration). The " decrease " in the dielectric constant which has been found experimentally may possibly be due to ionic effects, such as have been measured by Sack and Walden in experiments on solutions of electrolytes, or by van der Pol and Gutton in experiments on gases, and which may explain the propagation of short electric waves in the higher layers of the atmosphere.*

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* *Zeitschr. f. Physik*, **33**, 169 (1925).

† *Zeitschr. f. Physik*, **9**, 153 (1922).

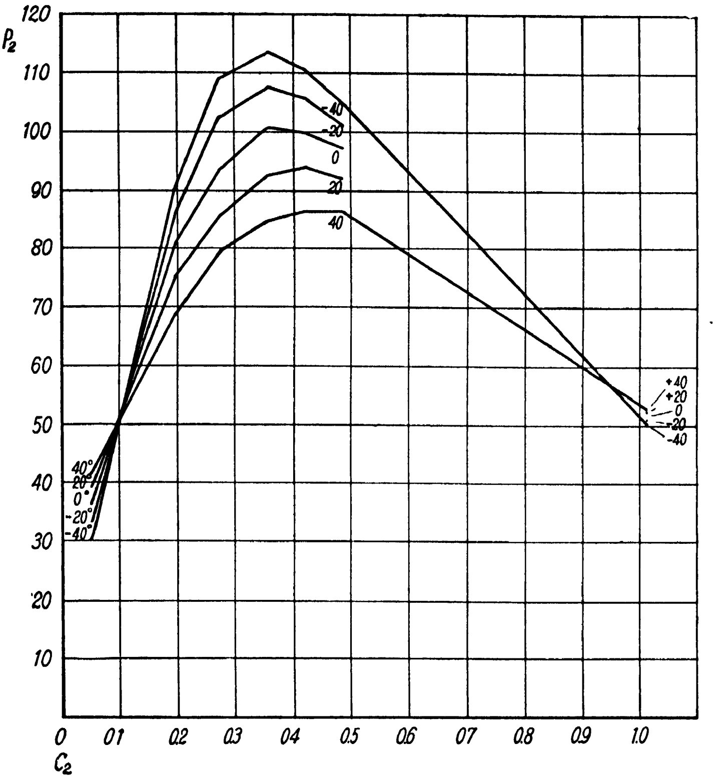

Fig. 3

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* For references to the literature see J. Errera, *Polarisation diélectrique*, Paris (1928).

The Dipole Moment and Molecular Structure

I. ESTERMANN, HAMBURG

The relationships which have hitherto been stated * to exist between the electric dipole moment and the structure of organic molecules may be summarized by the following rules:

I. The hydrocarbons have no electric moment or only a very small one.

II. If an H-atom of a hydrocarbon is replaced by another atom or radical, a moment is produced which is characteristic of the substituent in question ("group moment").

III. The moments of the substituents are to be regarded as vectors. If a molecule contains several substituents, the moment of the molecule may be calculated from that of the separate substituents by the rules of vector addition.

On closer investigation, however, it is found that rules II and III in particular are only in qualitative agreement with experimental results and fail to account for the latter quantitatively. In connexion with rule II we first notice that the moment is not constant for members of the same homologous series, but invariably depends on the hydrocarbon also, as Table I shows in the case of one or two substances.

TABLE I

DIPOLE MOMENTS FOR HOMOLOGOUS SERIES

Substance.	Moment.	Substance.	Moment.
CH_3Cl	$1{\cdot}86 \times 10^{-18}$	H–O–H	$1{\cdot}85 \times 10^{-18}$
C_2H_5Cl	$1{\cdot}99 \times 10^{-18}$	CH_3–O–CH_3	$1{\cdot}32 \times 10^{-18}$
		C_2H_5–O–C_2H_5	$1{\cdot}10 \times 10^{-18}$
		C_3H_7–O–C_3H_7	$0{\cdot}85 \times 10^{-18}$

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* See e.g. J. J. Thomson, *Phil. Mag.* (6), **46**, 497 (1923); Errera, *Journ. d. Phys.* (7), **6**, 390 (1925); Højendahl, *Phys. Zeitschr.*, **30**, 391 (1929); Smyth and Morgan, *Journ. Amer. Chem. Soc.*, **49**, 1030 (1927); Walden and Werner, *Zeitschr. f. phys. Chemie*, B, **2**, 10 (1929), &c.

The fact that rule II only holds qualitatively is also shown by the difference of the moments produced (especially in the case of halogens) when the substituent is introduced into an aromatic or an aliphatic residue. This is shown in Table II, which gives the approximate values of the group moments of various substituents in aliphatic and in aromatic hydrocarbons.

TABLE II

GROUP MOMENTS IN ALIPHATIC AND AROMATIC COMPOUNDS

Substituent.	Moment × 10^{18}.		Substituent.	Moment × 10^{18}.	
	Aliphatic.	Aromatic.		Aliphatic.	Aromatic.
F	—	− 1·4	CHO	2·7	− 2·8
Cl	2·0	− 1·5	NO_2	—	− 3·8
Br	1·9	− 1·5	OCH_3	—	− 1·0
I	1·7	− 1·3	COOH	—	− 0·9
OH	1·7	− 1·7	NH_2	1·3	1·5
CH_3COO	1·7	− 1·8	CH_3	—	0·4
— O —	about 1·0	about 1·0	CN	3·5	—
			— CO —	2·7	2·5

Rule III chiefly applies to multi-substituted benzene derivatives. If we assume that the six carbon atoms in benzene are arranged so as to form a regular hexagon, the angle between the directions of the substituents is 60° in the *ortho*-position, 120° in the *meta*-position, and 180° in the *para*-position. If the two substituents have the group moments μ_1 and μ_2, the moment of the di-substituted molecule is given by

$$\mu = \sqrt{(\mu_1^2 + \mu_2^2 + \mu_1\mu_2)} \text{ in the \textit{ortho}-position,}$$
$$\mu = \sqrt{(\mu_1^2 + \mu_2^2 - \mu_1\mu_2)} \text{ in the \textit{meta}-position,}$$
$$\mu = \mu_1 - \mu_2 \quad \text{in the \textit{para}-position.}$$

If the two substituents are the same, the formulæ may be simplified; we then have

$$\mu = \mu_1\sqrt{3} \text{ in the \textit{ortho}-position,}$$
$$\mu = \mu_1 \quad \text{in the \textit{meta}-position,}$$
$$\mu = 0 \quad \text{in the \textit{para}-position.}$$

In order to maintain agreement with experiment, it is necessary to associate a plus or minus sign with the group moment in the case of aromatic compounds, as is done in Table II. We find, for example, that the substituents NH_2 and CH_3 have an electrical effect opposite to that of the other atoms or radicals mentioned. Thus if we introduce into the benzene ring a group which is positive, in this sense, and one which is negative, the moment is least in the *ortho*-position and greatest in the *para*-position, whereas if the substituents have the same sign this order is reversed.

As regards the quantitative validity of rule III, Table III shows that here also there occur considerable deviations from the vector theory (which was first brought forward by J. J. Thomson).

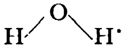
TABLE III

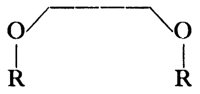
MOMENTS OF DI-SUBSTITUTED BENZENE DERIVATIVES

Substance.	$10^{18} \times \mu$ (observed).	$10^{18} \times \mu$ (calculated).
C_6H_5Cl	1·6	—
o-$C_6H_4Cl_2$	2·3	2·6
m-$C_6H_4Cl_2$	1·6	1·5
p-$C_6H_4Cl_2$	0	0
C_6H_5Br	1·5	—
o-$C_6H_4Br_2$	1·6	2·6
m-$C_6H_4Br_2$	1·1	1·5
p-$C_6H_4Br_2$	0	0
C_6H_5I	1·3	—
o-$C_6H_4I_2$	1·8	2·3
m-$C_6H_4I_2$	1·0	1·3
$C_6H_5NH_2$	1·6	—
$C_6H_5COOCH_3$	1·8	—
o-$C_6H_4NH_2COOCH_3$	1·0	1·7
m-$C_6H_4NH_2COOCH_3$	2·4	2·9
p-$C_6H_4NH_2COOCH_3$	3·3	3·4

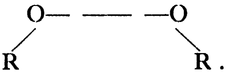
These discrepancies are still more marked in the case of some *para*-compounds where the two substituents are the same; according to the vector theory, these should have zero moments, whereas according to experiment they have moments of considerable size, namely:

Quinol diethyl ether $\mu = 1{\cdot}7 \times 10^{-18}$,
Quinol diacetate $\mu = 2{\cdot}2 \times 10^{-18}$,
Dimethyl ester of terephthalic acid $\mu = 2{\cdot}2 \times 10^{-18}$,
Diethyl ester of terephthalic acid $\mu = 2{\cdot}3 \times 10^{-18}$.

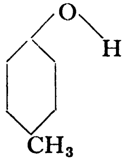
Various reasons are adduced for the deviations from the vector theory. J. J. Thomson himself drew attention to the fact that there may be forces acting between the substituents which affect their relative positions and thus change the angles between the group moments. If the substituent contains singly-linked oxygen, we must note in addition that the two valencies of the oxygen atom (if we use this diagrammatic notation) do not lie in one straight line. Even in the case of the water molecule we are led, as Hund has shown, to assume a triangular structure.* This is due to the fact that on account of the strong polarizability of the O-atom in comparison with the H-atom it is not the extended form of the molecule, H—O—H, that is stable, but the bent form . The moment of the symmetrical ethers is likewise to be ascribed to this "valency angle" in the oxygen atom. The greater the aliphatic residue of the ether, the greater is its polarizability. The result is that the molecule steadily approaches the extended form, so that the dipole moment decreases as the aliphatic residue increases in magnitude (cf. Table I, p. 27). According to Williams,† the large moments of the derivatives of quinol and terephthalic acid which we mentioned above are also to be ascribed to the valency angle in the oxygen atom. He therefore assumes that the quinol derivatives have the structure



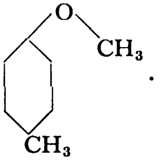
or



Fairly large deviations from the vector theory likewise occur in the case of the three cresols and the three cresyl methyl ethers; according to Williams these deviations are also to be ascribed to the etheric nature of the structure of these compounds, namely:



or



According to Højendahl the nitro-anisoles also exhibit very marked deviations from rule III, which may be explained in the same way.

In my opinion, however, the point of view described here, in which the substituents are regarded as fixed dipoles and the hydrocarbon residue as a neutral carrier, is not at all satisfactory. I prefer to regard the substituents as strongly distorted ions, which give rise to a displacement of the charges on the hydrocarbon residue and do not form a dipole unless in combination with this " distorted " residue. In chlorobenzene, for example, the dipole moment is not confined merely to the Cl-atom and the carbon atom attached to it, but extends over the whole molecule in such a way that there is an excess negative charge on the Cl-atom and an excess positive charge on the benzene residue. If there are several substituents, their polarizing effects on the benzene ring are superposed, and even in cases where the above-mentioned reasons for the deviations from the vector theory do not occur, it is by no means always necessary that the resultant total moment should be formed from the moments of the mono-substituted compounds according to the rules of vector addition. If, say, we are dealing with compounds with one positive and one negative substituent, e.g. an amino-acid, the centre of gravity of the positive charge lies in the NH_2-group, that of the negative charge in the COOH-group, and the magnitude of the moment depends on the distance between these two groups in the molecule, so that the moment increases in the order *ortho—meta—para*.

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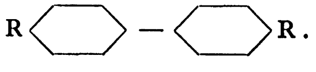
* F. Hund, *Zeitschr. f. Physik*, **31**, 81 (1924).

† J. W. Williams, *Phys. Zeitschr.*, **29**, 685 (1928).

Thus rule III cannot be used to determine the configuration of benzene derivatives in every case. In particular it is impossible to say right off from dipole moment experiments whether we are dealing with an *ortho*-, a *meta*-, or a *para*-compound. Some general statements about the structure of organic molecules may, however, be made as a result of dipole experiments. Apart from the result mentioned above, namely, that the two valencies of the " bridge oxygen " -O- do not lie in one straight line (a similar bend seems to occur in nitrogen also), the results of dipole experiments suggest very strongly that the six carbon atoms of the benzene ring lie in one plane. Besides the regularities already mentioned, the fact that the symmetrical compounds 1-3-5-trichlorobenzene and 1-3-5-trinitrobenzene have zero moments is an argument in favour of this configuration.

Definite statements about structure can also be made in the case of diphenyl compounds. Thus the moment is zero in *pp'*-dichloro-, dibromo- and dinitro-diphenyl, whence we may conclude that the two rings of diphenyl are arranged in one plane as shown below:



Some other *pp*′-derivatives of diphenyl with substituents containing oxygen are found to have moments of magnitude similar to those of the corresponding quinol derivatives, a fact which might likewise be explained by the valency angle of oxygen. Certain difficulties arise in the case of *pp*′-diamino-diphenyl (benzidine). The moment of this compound is found to be $\mu = 1{\cdot}3 \times 10^{-18}$, while the moment of the corresponding benzene compound, *p*-phenylenediamine, is found to be zero. Williams thought that this necessarily leads to the conclusion that in benzidine the two rings cannot possibly be in one plane, but that the structure of this compound must be thought of as bent or folded, so that the two benzene rings lie one above the other in two different planes. It was also thought that purely chemical arguments could be adduced to show that structures of this nature should be ascribed to numerous diphenyl derivatives. According to a remark made in the course of the discussion by Hückel, however, these chemical arguments are by no means conclusive, and according to another observation during the discussion by Debye the result for the moment of *p*-phenylenediamine is anything but certain, owing to the very slight solubility of this compound, so that *p*-phenylenediamine may possibly have a moment differing from zero also. Then the moment of benzidine might be explained by the valency angle in nitrogen, so that in the case of this molecule also it would be feasible to assume that the two rings lie in one plane.

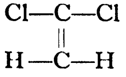
In all these arguments in which the " valency angle " plays a part it is assumed that the two polar substituents project on the same side of the plane of the ring. The effect of the field will lead to this arrangement provided the energy of the mutual action between the polar groups is small compared with the energy of the dipoles in the field and the groups are to some extent free to rotate about the single bond (cf. Ebert's paper, p. 43).

Some relationships between the dipole moment and molecular structure have also been found in the case of aliphatic compounds. In the first instance we may mention the two methyl esters of α- and δ-aminovaleric acid. We should expect from the results for the aminobenzoic acids that in an *open* chain the moment of the δ-ester would be greater than that of the α-ester, while in a chain joined into a ring the moments should be about the same. The values obtained are:

$\mu = 1{\cdot}6 \times 10^{-18}$ for methyl α-aminovalerate,
$\mu = 2{\cdot}7 \times 10^{-18}$ for methyl δ-aminovalerate,

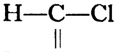
a result which is strongly in favour of the open chain structure.

A very important realm of application of dipole moments to the determination of chemical constitution is the *cis-trans* isomerism due to the presence of a double bond. For example, there are three isomeric dichloro-ethylenes, $C_2H_2Cl_2$, to which the structures *a*, *b*, *c* are ascribed.



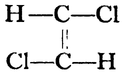
$$\begin{array}{c}\mathrm{Cl{-}C{-}Cl} \\ \| \\ \mathrm{H{-}C{-}H}\end{array}$$

a



$$\begin{array}{c}\mathrm{H{-}C{-}Cl} \\ \| \\ \mathrm{H{-}C{-}Cl}\end{array}$$

b (*cis*)



$$\begin{array}{c}\mathrm{H{-}C{-}Cl} \\ \| \\ \mathrm{Cl{-}C{-}H}\end{array}$$

c (*trans*).

While the configuration of the compound (*a*) can be definitely settled by its chemical reactions, this is not the case with the compounds (*b*) and (*c*). In general the assigning of each formula to its compound has been carried out in view of certain regularities in various physical constants: e.g. the compound with the higher boiling-point, the higher density, and the higher refractive index is taken to be the *cis*-compound. No theoretical relationships between these physical constants and the chemical constitution are available, however, so that this method of determining the configuration of a compound is extremely doubtful. Thus it is not to be wondered at that in many cases different authors assign formulæ to the compounds in different ways; for example, Walden and Werner * ascribe the *cis*-form to that dichloro-ethylene which Errera † calls the *trans*-form, and vice versa. Investigation of the dipole moment, however, enables us to determine the configuration uniquely: for in view of all the experimental material hitherto obtained we may safely assume that *trans*-compounds will have a very small moment, possibly even zero, whereas the *cis*-compounds will have a considerably greater moment, at least when there are no oxygen or nitrogen " bridges " in the molecule. Errera has made a number of measurements on the dipole moments of dihalogen compounds of ethylene (Table IV); according to these results the configuration which he previously assumed, and not that given by Walden and Werner, would appear to be the correct one.

In the case of the chloroiodo-ethylenes only I am inclined to throw doubt on the assignment of the formulæ given here. Errera ‡ follows the experiments of van de Walle and Henne, § who determined the positions of the atoms in these two isomers by chemical arguments. Errera now draws the conclusion from his measurements

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* Walden and Werner, *Zeitschr. f. phys. Chemie*, **111**, 465 (1924).

† Errera, *Phys. Zeitschr.*, **27**, 764 (1926).

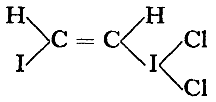
‡ Errera, *Phys. Zeitschr.*, **29**, 689 (1928).

§ Van de Walle and Henne, *Bull. Soc. Chem. Belg.*, **34**, 399 (1925).

TABLE IV

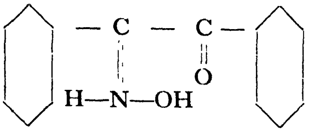
Substance.	Formula.	Moment × 10^{18}.
cis-dichloro-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{H{-}C{-}Cl}\end{array}$	1·9
trans-dichloro-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{Cl{-}C{-}H}\end{array}$	0
cis-dibromo-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}Br}\\ \Vert\\ \mathrm{H{-}C{-}Br}\end{array}$	1·4
trans-dibromo-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}Br}\\ \Vert\\ \mathrm{Br{-}C{-}H}\end{array}$	0
cis-diiodo-ethylene	$\begin{array}{c}\mathrm{H{-}C{-}I}\\ \Vert\\ \mathrm{H{-}C{-}I}\end{array}$	0·8
trans-diiodo-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}I}\\ \Vert\\ \mathrm{I{-}C{-}H}\end{array}$	0
cis-chlorobromo-ethylene ..	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{H{-}C{-}Br}\end{array}$	1·6
trans-chlorobromo-ethylene	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{Br{-}C{-}H}\end{array}$	0
cis-chloroiodo-ethylene (?) ..	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{H{-}C{-}I}\end{array}$	0·6
trans-chloroiodo-ethylene (?)	$\begin{array}{c}\mathrm{H{-}C{-}Cl}\\ \Vert\\ \mathrm{I{-}C{-}H}\end{array}$	1·3

that the iodine atom in the chloroiodo-ethylenes must be positively charged relative to the chlorine atom, and backs it up by the fact that an additive compound of chlorine and chloroiodo-ethylene exists, to which the structure

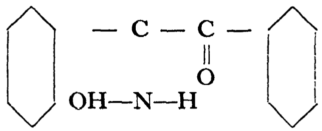


is ascribed. But, as we shall show later, in the case of *cis-trans* isomerism determinations of the configuration which are based on chemical reactions are very uncertain, and the assumption that the iodine atom has a positive charge relative to the chlorine atom seems to me to be incorrect for another reason. If we consider the corresponding benzene derivatives, we find that as a rule the *para*-compounds are analogous to the *trans*-compounds. Now iodobenzene has the moment $\mu = 1{\cdot}3 \times 10^{-18}$, bromobenzene $\mu = 1{\cdot}5 \times 10^{-18}$, and *p*-bromoiodobenzene $\mu = 0{\cdot}5 \times 10^{-18}$. It follows from this that the bromine and iodine atoms in the last-mentioned compound bear charges of the same sign (negative). As on the other hand bromine and chlorine bear charges of the same sign (also according to Errera's experiments on the chlorobromo-ethylenes), and there is no cause to assume that the iodine atom in the benzene residue has a charge different from what it has in the ethylene residue, I prefer to assign the *cis*-configuration to the compound with the moment $\mu = 1{\cdot}3 \times 10^{-18}$ and the *trans*-configuration to that with the moment $\mu = 0{\cdot}6 \times 10^{-18}$.

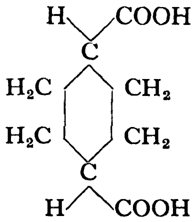
The determination of the configuration where *cis-trans* isomerism exists may also prove of great importance in other cases. Thus, for example, Meisenheimer * has shown that in the benzil oximes



and

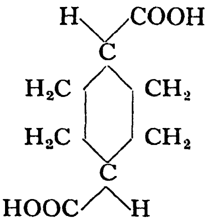


it is absolutely impossible to determine the configuration chemically, as according to the method used first one and then the other isomer must be regarded as the *cis*-form. Whether measurements of dipole moments will enable us to settle the question in the case of these particular compounds is meanwhile uncertain, but many other cases of *cis-trans* isomerism exist in which it will be possible to determine the configuration by means of dipole experiments. Thus Baeyer † found that the hexahydro-terephthalic acids exist in two forms,



(*cis*)

and



(*trans*)

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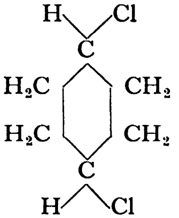
* Cf. the discussion in J. Meisenheimer and co-workers, *Liebigs Ann. d. Chemie*, **468**, 202 (1929).

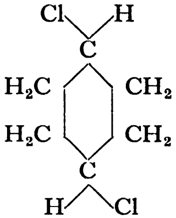
† A. v. Baeyer, *Ges. Werke*, I, 976 (Brunswick, 1905).

of which the *cis*-form should have the greater dipole moment. In this case, to be sure, the valency angle of the oxygen atoms in the COOH-group raises some difficulties, but the determination of the configuration would be unique in the case of the corresponding halogen derivatives,



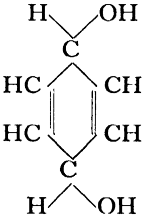
(*cis*)

and



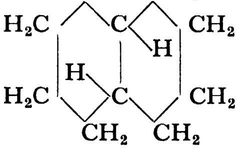
(*trans*)

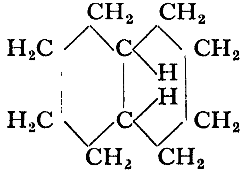
The quinols and their analogues, e.g.:



,

form another example of this kind of isomerism, in which it should likewise be possible to determine the configuration by means of dipole moments. A similar possibility may perhaps exist in the case of the dekahydronaphthalenes, among which Hückel * has distinguished the two isomers





as *cis*- and *trans*-forms. As the carbon atoms themselves have no moment, we should have to replace the hydrogen atoms in the middle e.g. by chlorine in order to obtain differences between the *cis*-form and the *trans*-form, and it is fairly unlikely that this substitution could be carried out under such conditions as would exclude the possibility of any change of configuration. In any case, however, it seems important definitely to establish the configurations of as many *cis-* and *trans-*compounds as possible by means of dipole experiments, for there is no doubt that we should then be in a position to discover new empirical relationships between the molecular configuration and the physical properties of the substances in question. In cases where the configuration cannot be found by a direct method we should then be able to determine it by means of these rules with much greater security than we can at present.

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* W. Hückel, *Liebigs Ann. d. Chem.*, **451**, 109 (1926).

Dipole Moments and Molecular Constitution

J. ERRERA AND M. L. SHERRILL,* BRUSSELS

The dipole moments of various aliphatic compounds containing one or more polar groups have been determined, but it seemed advisable to study the effect on the moment of the position of the polar group in an aliphatic compound.

In order to have several different positions available a study of some derivatives of heptane was begun. In the normal heptane it is possible to have a single substituent in four different positions in the molecule. The dipole moments of the four alcohols, heptanol-1 (*n*-heptyl alcohol), heptanol-2 (methyl-*n*-amyl-alcohol), heptanol-3 (ethyl-*n*-butyl-alcohol) and heptanol-4 (dipropyl-carbinol) have been measured.

Three of the corresponding chlorides, 2-chloro-, 3-chloro- and 4-chloro-heptane, and the four bromides have been synthesized. Great care was taken in the preparation of these compounds to avoid any shift of position in the chain. Additional compounds are to be studied.

The dipole moment of each of the compounds has been calculated from measurements of the dielectric constant of dilute solutions in a non-polar solvent, benzene, by the well known method given by Debye †.

The resonance method was used and the wave-length was 100 metres. The capacity measurements were of a precision of 1 part in 500.

It was not possible at this time to measure the refractive indices in the long waved infra-red, and instead of measuring $P_E + P_A$, P_E was determined from the refractive index of the compound obtained by measuring with the *He* yellow line at 20°. The data are tabulated below.*

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* C. R. B. Fellow, University of Brussels 1928–1929. An acknowledgment of an expression of appreciation for a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, which facilitated this work greatly, is hereby made.

† P. Debye, *Handbuch der Radiologie*, 6, 597, (1925).

Derivatives of Heptane

20°	Heptanol-1	Heptanol-2	Heptanol-3	Heptanol-4
d_4	0·8227	0·8167	0·8210	0·8183
ε	12·04	9·21	6·86	6·17
P	110·90	104·30	93·61	89·97
P_E	36·08	36·04	35·97	35·94
$\mu . 10^{18}$	1·7	1·7	1·7	1·7
20°		Chloro-2	Chloro-3	Chloro-4
d_4		0·8672	0·8690	0·8710
ε		6·54	6·69	6·55
P		100·43	101·44	100·12
P_E		39·50	39·47	39·40
$\mu . 10^{18}$		2·0	2·1	2·0
20°	Bromo-1	Bromo-2	Bromo-3	Bromo-4
d_4	1·1384	1·1277	1·1362	1·1351
ε	5·38	6·47	6·93	6·81
P	93·30	102·53	104·65	103·95
P_E	42·32	42·51	42·41	42·38
$\mu . 10^{18}$	1·8	2·1	2·0	2·0

The results show that in the case of the hydroxyl group in straight chain hydrocarbons, such as the heptanols, the dipole moment is independent of the position of the polar group in the chain. It is also to be noted that the association is greatest in the case of 4-heptanol, decreasing in order to 1-heptanol, which is least associated; for the dipole moment is the same for all four alcohols, and the density practically the same, yet the dielectric constant, which should be the same, varies from $\epsilon = 6·2$ in 4-heptanol to $\epsilon = 12·0$ in the case of 1-heptanol.

In the chlorides and bromides it is seen that in the 2-, 3-, 4-positions the dipole moment is practically independent of the position in the chain. In 1-bromo-heptane the dipole moment is slightly smaller than for the other bromides. The 1-chloro-heptane will be investigated for comparison. The dipole moment is the same for the chloro- and bromo-derivatives of the aliphatic compounds, as

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* P is the total polarization: $\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}$.

Williams * found for the chloro- and bromo-derivatives of aromatic compounds.

For disubstituted chlorides and bromides of benzene and of ethylene, one of us † has found that the moment of the chloro-derivatives is larger than that of the bromo-derivatives. In these aliphatic compounds the dipole moment of the chloro- and bromo-derivatives is greater than for the hydroxyl-derivative, in contradistinction to the aromatic compounds, where the dipole moment of the hydroxyl derivative is greater than that of the chloro- and bromo-derivatives.

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* J. W. Williams, *Journal Am. Chem. Soc.*, **50**, 2350 (1928).

† J. Errera, *Journal de Physique*, **6**, 390 (1925).

The Dipole Moment and Intramolecular Motions in large Molecules, especially in those of Aliphatic Compounds.*

L. EBERT, WÜRZBURG

I. Owing to the rapid growth both of chemistry (especially of stereochemistry) and of molecular and atomic physics, it has now become possible to obtain fairly detailed information about the structure of molecules. The following difference between the two lines of attack must, however, be borne in mind. Stereochemistry originated as an explanation of cases of isomerism, the differences between several molecules identical as regards chemical constitution and molecular weight being attributed to differences in the spatial arrangement of the atoms. It is obvious that this method is only available for molecules consisting of *several* (often of many) atoms, and that the geometrical structure of very simple molecules can only be inferred indirectly from the behaviour of their derivatives. Molecular physics, on the other hand, had perforce to start with substances which from the chemical point of view are very simple, and its methods were developed and tested by means of these comparatively straightforward atomic systems.

A number of different physical methods are now available for the investigation of these very simple molecules, and also to an increasing extent for more complicated molecules. To mention only the most outstanding of these, for the solid state we have the X-ray analysis of crystal lattices, and for the gaseous state the methods for determining molecular dimensions based on the kinetic theory of gases; of particular importance among the latter is the analysis of molecular spectra, which enables us to ascertain the moments of inertia of the molecule and also the individual vibrations possible within the molecule, and hence to investigate the nature of the intra-atomic forces.

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* The writer was engaged in preparing this paper for the *Zeitschr. f. phys. Chemie*, but had been delayed by external circumstances from completing it, when he received and accepted an invitation to take part in the *Leipziger Vorträge*, 1929. In this, the final form of his paper, he has been enabled to include results given in still more recent papers, the authors of which he desires to thank for their kindness in sending him proofs. Some of the most important points in the present paper are discussed from another point of view in joint papers by R. Eisenschitz and the writer.

Moreover, there exists a systematic method for deducing the degree of symmetry of the electrical structure of the molecule from purely physical measurements; a summary is given below.

Direction of increasing Symmetry in Electrical Structure
⟶

	$N_+ \neq N$ Ions.	$N_+ = N_-$ Neutral Molecules.		
		$S_+ \neq S_-$ Dipole Molecules.	$S_+ = S_-$ Electrocentric Molecules.	
			Anisotropic Molecules.	Isotropic Molecules.
Motion of a single molecule in a uniform field	Translation	Polar orientation (along the dipolar axis)	Apolar orientation (along the line of maximum dielectric constant)	—
Experimental phenomena	Ionic conduction: transport phenomena	Orientation polarization	Depolarization of scattered light	(All results negative)

N_+, N_- are the numbers of elementary positive and negative charges; S_+, S_- the centres of gravity of the different kinds of charges.

The conception resulting from the application of all the physical methods of investigation to the structure of very simple and in the chemical sense stable molecules may always be expressed by the following general statement. A *simple* molecule closely resembles a system of material particles possessing a well-defined position of equilibrium for which the energy of the system is a minimum.

If the molecule in this equilibrium position has a dipole moment, we shall call the latter the *natural* dipole moment of the molecule. The term " rigid " dipole moment * seems an unhappy one, seeing that " rigid " molecules really exist only as an ideal limiting case. Whether a natural dipole moment is rigid, i.e. not much affected by external conditions, is a question in itself, one which has often been raised and which is obviously of special importance in the case of substances with more than one dipole group.* Absorption and radiation of energy take place in accordance with the principles of the quantum theory. At a definite temperature the individual vibrations of the molecule itself are excited in proportion to their hardness or softness, i.e. in proportion to the magnitudes of the corresponding frequencies $\nu_1, \ldots, \nu_k$, and on the average molecules excited normally and otherwise will occur in the system under investigation in quantities proportional to the duration of the particular conditions of excitation associated with them. Provided the temperature is sufficiently low, by far the greater part of the molecules is always found to be in the normal state.

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* Ger. " *starres* " *Dipolmoment.*

In the language of classical dynamics and electrodynamics (which of course give the same results as the quantum mechanics in the case of slow vibrations) this means that any determination of the symmetry of molecules which form part of a collection of molecules arranged at random will in general give the symmetry of the *normal state* of the molecule, provided that we confine ourselves to sufficiently low temperatures.

If the molecule in this normal state has a natural electric moment μ, then—according to the theory of symmetry—its structure cannot be other than " polar ", i.e. it must have a polar axis. Hitherto, however, only fixed moments of the order of 10^{19} have been measured; it has not been found possible to determine numerically smaller polarities.

The question now arises what range of temperature must be selected in the case of any particular substance, in order that practically all the molecules dealt with shall be in the normal state. A molecule may of course exist in more than one relatively stable form, and in the case of complicated molecules we may expect several such configurations to occur. The geometrico-stereochemical ideas developed by Weissenberg † and Reis ‡ apply as strictly to molecules at sufficiently low temperatures as to molecules in solid crystal lattices, since in both cases we are dealing with configurations where the internal motions are confined to oscillations about positions of equilibrium. In actual fact the electrical symmetry of molecules is often investigated at temperatures at which the thermal motions are large in comparison with molecular dimensions. Two questions arise with especial reference to dipole experiments: (*a*) can internal vibrations of large amplitude give rise to polarizations which may be confused with polarization due to orientation? (*b*) Are the internal motions in the molecules such that high temperatures may cause a molecule for which $\mu = 0$ to acquire a genuine orientation polarization as a result of temperature effects?

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* L. Ebert, *Zeitschr. f. phys. Chemie*, **113**, 17 (1924): " a knowledge of the corresponding radical polarization might indicate to what extent they (i.e. the dipoles) are rigid ". In this section, which deals with substances having *several* dipole groups, the term P_A or P_R (loc. cit., p. 4, note 1) which is necessarily associated with every dipole can only refer to the relative motions possible between the individual dipole groups.

† K. Weissenberg, *Ber. d. dtsch. chem. Ges.*, **59**, 1526 (1926).

‡ A. Reis, *Ber. d. dtsch. chem. Ges.*, **59**, 1543 (1926).

Before discussing these problems, we shall consider the question whether the experimental methods used are liable to give rise to errors or difficulties in the interpretation of results. Two points are involved, (*a*) the *electric field* which it is necessary to use, and (*b*) the *duration of observation* characteristic of the method selected.

II. In criticizing any method for determining the symmetry of a molecule regarded as a configuration in which internal motions may occur, we must examine whether the method may not in itself have a tendency to alter the molecular structure owing to unavoidable effects on the molecules during its application. To take up an extreme position, it is objected that we can only make observations on the symmetry of molecules whose state has been markedly affected by the method of experiment, or, in our particular case, that the natural moment is readily disturbed and is therefore not rigid to any extent. Quantitative limits to this lack of rigidity are given below.

The only disturbing effect of this kind which is involved in the measurement of dipole moments results from the fact, which, to be sure, is unavoidable, that in these experiments the molecules are always subjected to an *external field*. The fields commonly used in measuring dielectric constants are comparatively weak and would exceed about 100 volts per centimetre in exceptional cases only. Stronger fields are used in the molecular-beam method, but hitherto this method has always given the same qualitative results as the other methods in common use. It is also known that even the highest strengths of field obtainable have only a very slight effect on the numerical values of the dielectric constants of pure liquids.

The effect of an electric field may *primarily* consist only in the alteration of the absolute value of μ in the field, i.e. an electrocentric molecule may acquire a noticeable induced moment γ in the field, or a molecule with a finite moment μ may in the field have a moment $\mu + \gamma$. We can now show a priori that this fact in itself can never give rise to a measurable orientation polarization P_0. The induced electric moments produced by fields below the sparking potentials of chemical substances are invariably very small compared with the natural electric moments which typical dipole molecules have experimentally been shown to possess. This question was fully discussed by Langevin * in connexion with his theoretical account of electrical double refraction (the Kerr effect).

Now every possible intramolecular vibration gives rise to a corresponding *vibration term* in P. According to the nature of the vibrations which it is possible to imagine taking place we shall, following earlier accounts, distinguish between three kinds of vibration term, namely:

Electronic polarization .. .. P_E,
Atomic polarization .. .. P_A,
Radical polarization .. .. P_R.

Whether the relative motions of whole radicals which are manifested in P_R are to be subdivided into " bendings " and " rotations " depends on the particular circumstances; practically it is more important to distinguish such motions by the extent to which they are damped.

Generally speaking, the moments γ_E, γ_A, γ_R induced by a field $E = 1$ e.s.u. $= 300$ volt/cm. are of the following magnitude (in rarefied gases and dilute liquids):

$$\gamma_E = \frac{3}{4\pi} \frac{1}{N} \cdot P_E = 4{\cdot}15 \cdot 10^{-25} P_E,$$

and correspondingly

$$\gamma_A = 4{\cdot}15 \cdot 10^{-25} P_A; \quad \gamma_R = 4{\cdot}15 \cdot 10^{-25} P_R.$$

$P - P_E$ may always be found by experiment, and in electrocentric molecules is exactly equal to $P_A + P_R$. According to our present knowledge, the maximum value of this difference may—if e.g. we take an unfavourable case and regard all observed differences $P - P_E$ as caused by large values of $P_A + P_R$—be taken as 1000. As a rule $P - P_E$ is very much smaller and frequently amounts to a few units only.† Thus we may as a safe limit put

$$\gamma_A + \gamma_R < 4 \cdot 10^{-22},$$

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* P. Langevin, *Le Radium*, **9**, 249 (1910); *Gött. Nachr.*, 1912, 589.

† For the magnitude of P_A see in particular the following: L. Ebert, *Zeitschr. f. phys. Chemie*, **113**, 5 (1924); **114**, 431 (1925); J. Errera, *Polarisation diélectrique*, Paris, 1928, p. 104; C. P. Smyth, *Journ. Amer. Chem. Soc.*, **51**, 2051 (1929).

and in most cases

$$\gamma_A + \gamma_R < 10^{-24}.$$

This shows how small these induced moments are compared with the natural moments of typical dipole molecules, which are greater than 10^{-18}. From the values of γ_A and γ_R we may estimate the absolute amounts of relative displacement of parts of the molecules caused by a given external field, including both the extension of a simple dipole, like e.g. that of the HCl molecule, and the bending or twisting of larger parts of molecules, which may comprise whole dipole groups. The changes in the distances or angles between polar groups remain small as compared with the dimensions of a molecule even for the highest potential differences available, say 300,000 volts/cm. = 1000 e.s.u. Even in these extreme cases, of course, the electrical energy stored up in a molecule is only a small fraction of the mean kinetic energy per degree of freedom at $T = 300$, and a still smaller fraction of the total thermal energy of the molecule. The amplitudes of the vibrations of radicals say at room temperature may reach the order of 10^{-9} cm. under representative conditions. Hence there exists a natural upper limit to the value of $P_A + P_R$; too high a value of $P_A + P_R$ would involve thermal amplitudes which even at low temperatures would pass beyond the limits of stability of the molecules and would thus give rise to rapid thermal decomposition.

To each vibration term P_E, P_A, P_R, there must, in so far as the molecule concerned is *anisotropically* polarizable with respect to the vibration in question, correspond an orientation term (" induced orientation polarization "). The molecules tend to set themselves with the axis of maximum polarizability in the direction of the external field. Even in the most favourable cases the absolute values of these contributions to P_o are, as we shall show by an example, practically negligible. For a vibration so markedly anisotropic that as compared with the value γ_1 for the " softest " direction of the molecule the two other values γ_2, γ_3 vanish, Langevin's formula (see reference on p. 47) gives the expression

$$(P_o)_{\text{induced}} = 0{\cdot}65 \,.\, 10^{-24}\, P^2 E^2$$

for a substance in dilute benzene solution. Even for the maximum possible values $P = 1000$ and $E = 1000$, $(P_o)_{\text{induced}}$ is only of the order 10^{-12}, i.e. vanishingly small.

Thus of all polarizations due to orientation only those of natural dipoles give a measurable effect, and then only when μ exceeds the order of 10^{-19}. At present there is no experimental method suited to the detection of natural moments less than 10^{-19}, and this would still have to be divided by several powers of ten to reach the magnitude of ordinary induced moments.

An external field may have a *secondary* effect, namely, the induced moment γ may cause certain vibratory motions, which in the undisturbed molecule are symmetrical, to become *unsymmetrically* anharmonic. Here by symmetric anharmonic vibrations we mean those for which the energy Φ is an *even* function of the distance x:

$$\Phi = \tfrac{1}{2}ax^2 + \tfrac{1}{4}cx^4 + \dots .$$

The energy of unsymmetrical vibrations contains odd powers of x in addition. It is only in these unsymmetrical vibrations that, apart from the change of frequency which always occurs in anharmonic vibrations even in the symmetric case, change of amplitude results in a displacement of the centre of the vibration.

A special instance of this effect has recently been discussed by G. Jung and A. Schleede.* Here it is not a case of the production of polarization due to orientation, but of the occurrence in a vibration term of a correction depending on the temperature. Theoretically speaking, this term may equally well be positive or negative (for further details see below), and to a first approximation its numerical value increases linearly with the absolute temperature.

It is important to remember that here we are dealing with a vibration term, i.e. in all cases with moments of small order of magnitude (because they are induced) which, by what we have said above, can never give rise to a measurable contribution P_o. There are several ways of determining whether a considerable part of P is derived from vibration terms of this kind, i.e. whether an observed variation of P with temperature is to be attributed to a correction term in $P_A + P_R$ depending on the temperature. We now proceed to consider the usual methods for evaluating dipole moments.

Obviously no method which only gives the *difference* $P - P_E$ for *one* temperature can make any contribution to the question under discussion unless with the help of fresh information from another source. If, for example, we observe P_{solid} in addition,† the difference $P_{\text{solid}} - P_E$ gives the sum of all the vibration terms $P_A + P_R$

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* G. Jung and A. Schleede, *Zeitschr. f. phys. Chemie*, B, **4**, 207 (1929).

† As is well known, P_{solid} can only be calculated from the expression $\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d}$ when the crystals of the substance are not too markedly anisotropic.

for the *solid* body. In addition to terms representing vibrations within the molecule this difference includes terms representing intermolecular vibrations, the frequency of which, according to Lindemann, is related to the melting-point of the substance.* Hitherto it has been found that for all substances for which $P - P_E$ is large the difference $P - P_{\text{solid}}$ is also large, i.e. the sum $(P_A + P_R)_{\text{solid}}$ is comparatively small. If, then, we desire to express the whole difference $P - P_E$ in the state of solution, which, as is well known, agrees the more closely with the value for the vapour the more reliable the measurements are, as a sum of vibration terms $P_A + P_R$, we are forced to assume that the frequencies of the corresponding vibrations in the molecule are *much* larger than for the molecule in the amorphous condition. For equal masses moved, in fact, the relationship $P \sim 1/\nu^2$ is approximately true. The information hitherto available about the frequencies of intramolecular vibrations, which of course occur only rarely in the region of the remote infra-red, would rather indicate that intramolecular frequencies depend only to a slight extent on the state of aggregation. To this extent a knowledge of P_{solid} provides a contribution to the discussion of the nature of the difference $P - P_E$. To refer again to the special case of the group of substances $C\alpha_4$, the molecules for which the difference $P - P_E$ is large also have the difference $P - P_{\text{solid}}$ large.

The investigation of the way in which P depends on the *temperature* offers a better prospect, from the theoretical point of view, of distinguishing between the vibration terms and genuine orientation polarization, provided we can neglect the correction terms in P_E, P_A, and P_R which depend on the temperature. As a further source of disturbance † there may, of course, also arise the "uncoupling" of remote parts of the molecule, which will increase in extent with rise in temperature. As long as the temperature variation of P exhibits only variations from the simple law

$$P = A + \frac{B}{T},$$

some one definite explanation can usually be adopted as being the simplest and most probable one. If the deviations are greater the choice between the various possible explanations remains open. In addition to those already mentioned, there is also the possibility that for a definite range of temperature there may exist a state of equilibrium, varying with the temperature, between several configurations of a complicated molecule, each of which has its own electric moment μ. Such assumptions have already been made by Tammann [*] in order to explain polymorphism, and more recently to explain the rotatory dispersion of optically active substances.[†] It is just on account of all these possible complications that it becomes very important that we should observe the variation of P with temperature in complicated molecules, in order that we may at least ascertain the magnitude of the deviation from the normal in each particular case, even if a definite interpretation of it can in many cases be obtained only with the help of other independent methods.

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* D. H. Andrews, *Leiden Commun. Suppl.*, No. 56 (1926) also assumes the existence of rotatory vibrations of large molecules in the fixed lattice in his explanation of specific heats (see also E. Schrödinger, *Handbuch der Physik*, **10**, 314, note 2).

† Here we do not consider disturbing effects due to association, which in theory may always be avoided by making the concentration sufficiently small.

It is urgently necessary that the methods for distinguishing between vibration and orientation terms should be extended to the closer investigation of the dispersion curves of large molecules in the region between $\lambda = 10\mu$ and $\lambda = 100$ cm.[‡]

All these methods have the fundamental defect that we merely obtain quantities of the same nature (which are essentially positive contributions to P) and it is only by investigating their properties in greater detail—e.g. by finding the temperature variation or dispersion curve for each term—that we are enabled to separate these essentially different kinds of term.

In this respect the molecular-beam method [§] has a marked advantage. All induced moments, no matter what their nature, give rise in the non-uniform field used to a deviation of the molecular beam in *one* direction. An induced moment, of course, is always in the " right " direction and the molecule rotates about the direction of this induced moment. If, however, there exists a natural dipole moment of magnitude at least equal to several units of order 10^{-19}, a different effect arises, namely, a *broadening* of the molecular beam on either side to an extent which can be measured.

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[*] See G. Tammann, *Aggregatzustände* (Leipzig, 1922), p. 140 *et seq.* See also the important paper by K. Schaum, *Ann. d. Chem.*, **462**, 194 (1928), which gives references to the older literature.

[†] See e.g. R. Lucas, *Comptes rendus*, **182**, 378 (1926); L. Longchambon, *Comptes rendus*, **182**, 769 (1926).

[‡] See *Zeitschr. f. phys. Chemie*, **113**, 8 (1924); B, **1**, 112 (1928). I should like to take this opportunity of expressing my regret that the work on these lines which I had planned to undertake along with G. Laski has been cut short by the death of this accomplished worker. I am glad to find that Errera has announced similar experiments (*Physik. Zeitschr.*, **29**, 690 (1928).

[§] See I. Estermann, *Zeitschr. f. phys. Chemie*, B, **1**, 161 (1928), and the paper in this book (p. 15).

At present, therefore, this method is the best way of testing whether, in the case of any particular molecule, the greater part of the difference $P - P_E$ or $P - P_{\text{solid}}$ may be ascribed to a genuine orientation polarization with a moment $\mu > n \,.\, 10^{-19}$, say, or whether the difference is probably traceable solely to contributions $P_A + P_R$, the variation of which over a small range of temperature cannot in an unfavourable case be distinguished very clearly from that of a term of the type P_o.

In due course this led us to ask Dr. Estermann to investigate some suitable substances of the type $C\alpha_4$ by the molecular-beam method. These experiments have definitely confirmed our interpretation of the differences $(P - P_E)_{\text{solution}}$ or $P - P_{\text{solid}}$ as genuine terms of the type P_o. All the substances for which we obtained differences of considerable size give a correspondingly large genuine term P_o by the molecular-beam method. The discovery that $C(CH_2Br)_4$, which at low temperatures is non-polar, still remains so at the much higher temperatures of the molecular beam is of special importance.*

To sum up, the effect of an external field, i.e. the production of induced moments in molecules, whether the latter depend on P_E, P_A, or P_R, can never give rise directly to a measurable contribution P_o. Theoretically an external field may indeed render anharmonic vibrations unsymmetrical and thus give rise to a measurable effect (see further below), but according to experiments by the molecular beam method this effect can only be made to account for a trifling part at most of the observed differences $P - P_E$ or $P - P_{\text{solid}}$ in the dipole molecules $C\alpha_4$ which were investigated.

III. Apart from the external field used, every method for observing molecular symmetry has a definite and characteristic *duration of observation*, which we shall define as the average length of time for which a molecule can remain in an external field of the same direction. This length of time Θ may be limited (*a*) by the period of alternation of the external field, (*b*) by the rotation of the molecules themselves.

(*a*) If in the first instance we neglect the rotation of the molecules themselves, e.g. in viscous fluids, Θ is equal to the half-period of the external alternating field used to measure the dielectric constant. In general we have the theorem that for all periodic intramolecular motions for which the period $\tau_{\text{per.}} \ll \Theta$ the method only registers the induced moments of the *appropriate* position of equilibrium (which in theory may depend on the external field and on the temperature). By arguments analogous to the previous discussion of the connexion between the maximum value of the terms $P_A + P_R$ and the thermal stability of a molecule, it may be shown that for periodic intramolecular motions (even of large parts of the molecule) frequencies below $0{\cdot}5 \,.\, 10^{12}$ (i.e. wave-lengths above 600 μ) are in general to be regarded as exceptional.* If, then, we work with wave-lengths exceeding 1 metre, the asymmetry due to thermal vibrations in a single direction will not in general be recorded.

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* As the results of these experiments have not yet been published in detail, we may mention that the following compounds have definitely turned out to be polar in the molecular beam: $C(CH_2OH)_4$, $C(CH_2O_2C\,.\,CH_3)_4$, $C(COOCH_3)_4$, whereas $C(CH_2Br)_4$ is non-polar.

Aperiodic motions, whether intramolecular or consisting of an orientation of the molecule as a whole, are characterized by their respective relaxation times $\tau^{i}_{\text{aper.}}$ and $\tau^{\text{mol.}}_{\text{aper}}$. According to Debye † we may in general expect $\tau^{i}_{\text{per.}}$ to be less than $\tau^{\text{mol.}}_{\text{aper.}}$, as $\tau^{\text{mol.}}_{\text{aper.}}$ is of about the order of 10^{10} second. But even for the possible exceptional case where $\tau^{i}_{\text{per.}} > \tau^{\text{mol.}}_{\text{aper.}}$ the general statement that the moment of the equilibrium position is alone observed still remains true, provided only that $\Theta > \tau_{\text{per}}$. During the time Θ the molecule then proceeds to execute many vibrations of frequency $c/\tau_{\text{per.}}$; during the one phase of its periodic vibration it will set itself to one side but will then automatically swing back and will thereby be re-oriented, so that over the long period Θ it will make as many positive contributions to P as negative. Very slow periodic vibrations within the molecule have the further result that each vibration gives rise in the dispersion curve to an effect more or less like that shown by curve I in fig. 1 in the neighbourhood of $\nu_{\text{per.}} = c/\tau_{\text{per.}}$ but one like that shown by curve II in the neighbourhood of $\nu_{\text{aper.}} = c/\tau_{\text{aper.}}$. Thus if we have reason (say on account of the unsuspected asymmetry of a particular molecule) to suspect that what is being recorded is not the natural moment but the moments of the single—and obviously very unsymmetrical—phases of slow internal vibrations, then in passing gradually to longer and longer waves we must necessarily traverse a region like curve I; i.e. noticeable dispersion must be exhibited. Dispersion curves of form I are not known experimentally for waves longer than a few decimetres in the case of liquids and gases. Even very slow vibrations can be detected in this way by choosing Θ sufficiently long.

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* The question whether the dispersion bands observed with feebly damped waves by Colley, Obolensky, Romanoff, Potapenko, and others (*Handbuch der Physik*, **15**, 514 *et seq.* (Berlin, 1927)) in the region of wave-lengths of a few decimetres correspond to intramolecular vibrations might be determined by comparison of the spectra of the *vapours* with those of the liquids. As is well known, the kinetic theory of liquids has recently exhibited a decided tendency to follow the theory of crystal lattices more closely in many respects; for a comprehensive account of some of the most important papers on this subject see K. Jellinek, *Lehrbuch der physikalischen Chemie*, **1**, 824 *et seq.*, especially pp. 828, 831 (Stuttgart, 1928).

† P. Debye, *Ber. d. dtsch. phys. Ges.* **15**, 777 (1913); *Polare Molekeln*, pp. 88 *et seq.* (Leipzig, 1929); *Polar Molecules*, pp. 77 *et seq.* (New York, 1929).

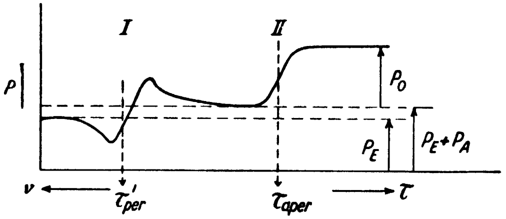

Fig. 1

We shall also give a special discussion from this point of view of the attempts to explain dipole moments which do not correspond to the equilibrium configuration at low temperature by the freedom of whole parts of the molecule to rotate relative to one another. Here the damping of the motion plays a very important part. In the case of small molecules we can scarcely risk an a priori assumption about this. If the motion of a small group chiefly takes place in such a way that the group practically remains in the neighbourhood of the molecule it may still be preferable to regard the motion as vibratory. But the motions of more remote parts of large molecules e.g. in a solution are chiefly motions relative to the molecules of the solvent, and therefore motions taking place in viscous fluids, particularly motions of exposed parts of the molecules relative to one another, may (like the rotations of the molecules as a whole) be strongly damped and hence aperiodic. Thus if the individual dipole groups in a molecule are free to move relative to one another they may in the limiting case where their mutual effect is trifling behave almost like single independent dipoles. We shall have to discuss this limiting case in greater detail later. Even here, however, we see that in molecules where the individual dipoles are very close together, as e.g. in the dipole molecules $C\alpha_4$ (e.g. $C(CH_2OH)_4$) the single group must in general behave as a dipole does in surroundings which are very rich in dipoles. A comparatively strong and in certain circumstances strongly anisotropic [*] molecular field will have to be taken into account, similar in strength, no doubt, to the field in the interior of a uniform liquid containing a large number of dipoles, where the nearness of the individual dipoles to each other leads to well-known anomalies in the behaviour of dielectrics. In the case of individual dipoles these phenomena may be roughly explained by the idea of products resulting from association, so long as we are unable to work out the statements proposed by Debye [†] on the grounds of molecular theory quantitatively. Dipole effects, however, are by no means the sole source of noticeable internal fields. Among the causes of such fields must be reckoned any constraint on the motion of the dipole relative to the molecule, arising e.g. from the occurrence of favoured valency angles, polarization effects along the chain, &c.[‡] Thus the determination of dipole effects alone will in general merely give a *lower* limit for the internal field. As a rule, therefore, single groups free to move will behave as if they were subject to a constant field, i.e. the directional effect of an external field upon them will be greatly diminished—a sort of dielectric saturation in the internal field. Provided $\Theta \gg \tau_{\text{aper.}}$, that orientation of the individual dipole groups which corresponds to their probable positions in the combined external (experimental) and internal (molecular) fields will always be manifested in P_o. The effect of the internal field, and hence of the observed polarization due to orientation, may depend very largely on the temperature if the energy of the field is comparable with the mean temperature energy. This fact may aid in the detection of the phenomenon. In this intermediate region, however, it is also possible to give an explanation of the phenomena in which the same definite moment is no longer assigned to each whole molecule (as is necessary e.g. in the case of HCl) but where the molecules in a certain region have random moments differing widely amongst themselves. The development of an experimental method to enable us to distinguish between these two cases *directly* would be extremely desirable. In connexion with the molecular-beam method we remark in conclusion that in its case the length of time during which the external field acts on a molecule in one direction is limited by half the mean period of rotation ($\tau'_{\text{rot.}}$) of the molecule. All vibrations for which $\tau^i_{\text{per.}} < \tau_{\text{rot.}}$ contribute the full values γ_E, γ_A, &c., to the deviation of the beam to one side. If rotations occur independently of each other within isolated molecules, the resultant moment of the whole molecule will not have a *single* definite value but will assume a number of values for μ. If there is an internal field the resultant moment will depend in this case also on the competition between the internal and external fields.

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[*] The meaning of this anisotropy requires closer discussion from the quantitative point of view; a paper on this subject by L. Ebert and R. Eisenschitz is expected to appear in a forthcoming number of *Zeitschr. f. phys. Chemie.*

[†] P. Debye, *Handbuch der Radiologie*, **6**, 637 (Leipzig, 1925).

[‡] This polarization along aliphatic chains forms the only explanation of the dissociation constants of organic acids, in particular of the effect of substituents, and must also, according to N. Bjerrum (*Zeitschr. f. phys. Chemie*, **106**, 220 (1923)), be taken into account in the theoretical explanation of the dissociation constants of polybasic acids. Quantitative limits to the magnitude of this effect may be obtained by experimenting with different solvents (L. Ebert, *Ber. d. dtsch. chem. Ges.*, **58**, 175 (1925)); for short chains its value is found to be considerable.

IV. The effect of *temperature* on all the different possible intramolecular motions can only be determined quantitatively to a trifling extent. Hence in what follows we can only select a few important considerations for discussion; these chiefly relate to the question whether internal motions are capable of giving rise at high temperatures to a genuine orientation term in the case of molecules which at low temperatures are non-polar.

(*a*) As we have already observed above, a genuine contribution P_0 can in theory be detected with certainty by means of the molecular-beam method. But seeing that it is only practicable to apply this method in the case of a few substances and that it is not yet completely developed from the quantitative point of view, we shall begin by discussing the effect of those anharmonic *vibration terms* which either are already unsymmetrical in the normal state of equilibrium of the molecule or become unsymmetrical as a result of the inductive effect of the external field. In theory the absolute value of these terms may be large enough to give rise to confusion with contributions P_0 corresponding to appreciable moments μ. (As we have said above, such confusion is possible in the measurement of $P - P_{\text{solid}}$ only where vibrations occur which give rise to far smaller contributions $P_A + P_R$ in the solid state than in the amorphous states.)

For any vibration term which is unsymmetrically anharmonic we have the relationship

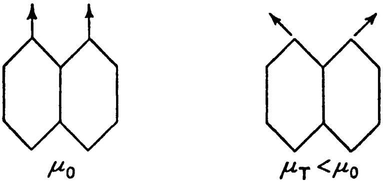
$$P = \frac{4\pi}{3} N (\gamma + \Delta\gamma_T)$$

where γ is the induced moment for $E = 1$ and is practically always so small that in describing the motion of the system we may still assume that the motion is simple harmonic, and $\Delta\gamma_T$ is the change in the moment due to the displacement of the centre of the vibration for large amplitudes. As is immediately obvious from the following examples, $\Delta\gamma_T$ may be positive or negative according to the nature of the vibration. The absolute value of $\Delta\gamma_T$ increases linearly with the absolute temperature.

(1) The vibrations of a *simple* dipole *AB* of unit length will result in an *increase* in the mean interval 1 for large amplitudes, just as when crystal lattices expand as the result of heat; $\Delta\gamma_T > 0$.

(2) The vibrations of a resultant dipole which is formed by geometrical combination of several charges or several separate dipole groups may likewise only affect an equilibrium position of these separate parts in such a way that the *linear dimensions or angles increase* with higher temperatures; in general, in such a way that the movable parts are displaced into regions where the curve of the potential of their mutual effect is flatter. In this process the resulttant moment may just as well increase as decrease, according to the structure of the molecule. An example of each case is given in fig. 2, where we are dealing with vibrations which are unsymmetrical apart from external influences. Jung and Schleede * have worked out an example for bending vibrations which is in itself symmetrical but becomes unsymmetrical as a result of the inductive effect of an

(*a*) Decrease of μ



(*b*) Increase of μ

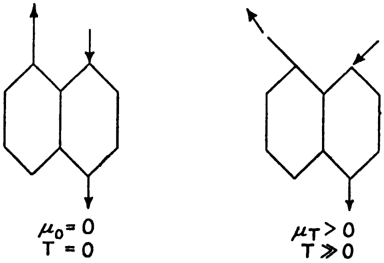


Fig. 2

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* G. Jung and A. Schleede, *Zeitschr. f. phys. Chemie*, B, 4, 207 (1929).

external field, and have reached quantitative conclusions which render it probable that the effect in question forms part of the explanation of large differences $P - P_E$.*

In actual fact, however, there is as yet no indication of a confirmation of this assumption even in the case of the most suitable organic molecules, in so far as they have been investigated with sufficient accuracy. Special mention must be made in this connexion of some very good recent experiments on the vapours of symmetrical ethers. Two entirely independent series of measurements by Stuart † and Sänger ‡ turn out to be excellent examples of the validity of the ordinary form of Debye's law (equation (1), p. 2), over a wide range of temperature. In the case of the largest molecule investigated (dipropyl ether), however, the term $P_A + P_R$, according to Sänger,‡ is much larger than for the two lower homologues, but there is no indication of an abnormal temperature variation. Measurements of P as a function of the temperature for sufficiently complicated organic molecules have been carried out by Estermann. § He uses dilute benzene solutions of higher aliphatic ethers, aromatic-aliphatic ethers, and a number of benzene derivatives containing several groups, sometimes very large ones. The *simple* temperature relationship is found to hold equally well in all the cases investigated. Hence large-scale effects of the kind assumed by Jung and Schleede certainly do not occur in this fairly varied selection of molecules, although the structure of some of them may be regarded as specially adapted to give rise to such an effect.|| Besides, all the substances which it was found possible to investigate by the molecular-beam method exhibit a moment under those conditions which is pretty nearly of the same magnitude as would be obtained simply by interpreting the difference $P - P_{\text{solid}}$ as an orientation term. The agreement with the moments calculated from dP/dT is even better.

This result, in fact, forms a fairly far-reaching argument against the assumption that in sufficiently complicated molecules there could exist large contributions $P_A + P_R$ peculiar to the amorphous states

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* The quantitative details of this calculation lead to various conclusions which have been objected to, but we shall not go into the matter here.

† H. A. Stuart, *Zeitschr. f. Physik*, **51**, 490 (1928).

‡ R. Sänger and O. Steiger, *Helv. phys. Acta*, **2**, 136 (1929), and R. Sänger's paper in the present book (p. 1).

§ I. Estermann, *Zeitschr. f. phys. Chemie*, B, **1**, 134, 422 (1928).

|| W. Lautsch, *Zeitschr. f. phys. Chemie*, B, **1**, 129 (1928) obtains the correct temperature effect even for *very large* ester molecules.

in contradistinction to the solid state. Nevertheless it is highly desirable that the matter should be investigated independently from the accurate quantitative point of view. As an example of abnormal variation with temperature in the case of the vapour of a large molecule we may consider Maske's experiments on benzophenone.* Here, however, we have the following state of affairs; the value of P for Maske's *highest* temperature is in satisfactory agreement with the value obtained from Estermann's value of the temperature variation of P for the substance in solution (Maske obtains the value $P = 169$ at 336° C. and Estermann's calculations give 167·5). Maske's values for low temperatures are too high, but the higher the temperature the more closely do they approach the values anticipated, i.e. the anomaly in the temperature variation diminishes with increase of temperature, a fact which contradicts the fundamental idea of the proposed mechanism. The phenomenon is perhaps most simply explained by chain association at low temperatures. The only really abnormal temperature variation of a term $P - P_E$ of considerable magnitude hitherto discovered is Werner's result for quinol diethyl ether.† In comparison with Estermann's varied material this is meanwhile an isolated phenomenon and requires closer investigation.

(*b*) The effect of thermal motions on the *genuine* orientation polarization P_0—calculated for a molecule as a whole—may have very different values, according to the magnitude of the internal field associated with the particular group.

An extreme case is represented by the following model: several (e.g. two) dipole groups belong to the same molecule, but the effect of the internal field of the molecule on each dipole is extremely small. Two groups say at the ends of a very long chain could behave as if they were loosely connected as if by string.‡ Then the only constraint on their motion is the condition that the distance between the two groups can never exceed the length of the tie joining them when fully extended. If we have N such kinetic molecules and if in the individual molecule there are $\nu_1, \nu_2, \ldots,$ such independent dipole groups of different kinds with moments $\mu_1, \mu_2, \ldots,$ the N molecules together behave as if there were ν_1 molecules of moment μ_1, ν_2 molecules of moment μ_2, &c., all practically independent of each other. In this case, therefore, we have

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* F. Maske, *Physik. Zeitschr.*, 28, 533 (1927).

† O. Werner, *Zeitschr. f. phys. Chemie*, B, 4, 393 (1929).

‡ Such an assumption really goes too far to be applied to any actual molecule, as of course even remote parts of an isolated large molecule must in general exert the universal van der Waals attractive forces on each other at least (see further below).

$$P_o = k\frac{N}{T}(\nu_1\mu^2 + \nu_2\mu_2^2 + \ldots).$$

The simplest case is that given above, namely, where two groups of the same kind occur in one molecule. Then

$$P_o = k\frac{N}{T} \cdot 2\mu_1^2.$$

The apparent moment of a molecule of this type is therefore $\sqrt{2}\mu_1$. We shall speak of a molecule which contains several practically independent dipole groups and behaves as described above as " ideally uncoupled ". Now if the internal field is sufficiently small the moment of any molecule with several dipole groups can only change with rising temperature in such a way that it approaches the value for the *ideally uncoupled molecule.* It may happen that the molecule does not actually attain this imagined limit owing to its undergoing thermal decomposition before reaching it, but this will make no difference to the direction in which μ varies with temperature. Then the electric moment of the molecule will *increase* or *decrease* with temperature according as the value of μ for the configuration which exists at low temperatures is less than or greater than the value for the ideally uncoupled state.

If, then, we are to explain the temperature variation of μ by means of this process of gradual uncoupling, definite relationships must hold between the absolute magnitude of the moment (as compared with the value for the ideally uncoupled state) and its temperature coefficient. This very point would seem to lead to difficulties in connexion with the results of Werner which we mentioned above. In the ideally uncoupled state quinol diethyl ether should have the moment $\sqrt{2}\mu_1$, where for μ_1 the value for phenetole ($1{\cdot}0 \,.\, 10^{-18}$) should be inserted.* In this way we obtain $1{\cdot}4 \,.\, 10^{-18}$ as the limiting value for the ideally uncoupled state, i.e. a number which is *smaller* than the moment obtained experimentally for the di-derivative ($1{\cdot}7 \,.\, 10$ ^{18} at 20° C.). Now with rising temperature Werner does not obtain the anticipated tendency towards the limiting value but a further increase in the moment, which obviously makes an explanation of the phenomenon difficult. We may add that the only possible way of explaining Werner's result by the mechanism of unsymmetrical anharmonic vibrations seems to be to give the individual vectors in the molecule the relative positions shown in fig. 3; but this is in contradiction with the angles given by classical stereochemistry, which Wolf proposes to take for granted.*

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* I. Estermann, *Zeitschr. f. phys. Chemie*, B, **1**, 153 (1928) gives $\mu = 1{\cdot}0 \,.\, 10^{-18}$ from experiments on P as a function of T in benzene solution. As Højendahl has obtained a considerably larger value for anisole ($1{\cdot}16 \,.\, 10^{-18}$) than Estermann did ($0{\cdot}8 \,.\, 10^{-18}$, loc. cit.), it would be desirable to have the value for phenetole confirmed.

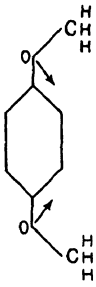

Fig. 3

As regards the substances of type Ca_4 recognized to be polar molecules, we can (in view of the perfectly definite results of the molecular-beam method) only adduce the process of partial uncoupling of individual groups as an explanation of the observed differences $P - P_{\text{solid}}$ if we regard these values not as natural moments of a definite equilibrium position but as caused by intramolecular motions. Thus if we are dealing with the state of transition to the highest possible degree of uncoupling, the observed moment in the case of these substances—provided that, starting from the well-known basis of ordinary stereochemical ideas, we assume that the natural moment is zero—can only *increase* with increase of temperature. This statement, be it noted, is qualitatively in contradiction with the result for the temperature variation of the difference $P - P_{\text{solid}}$ which Jung and Schleede deduce from the mechanism proposed by them.

In connexion with this question, it may be mentioned that the considerable rise of temperature over that of the room necessitated in the use of the molecular-beam method does not, so far as we know at present, have any appreciable effect. The molecule $C(CH_2Br)_4$ is of special significance; according to classical ideas it should certainly have its individual dipoles inclined to the C — C linkages similarly to the individual dipoles in $C(OCH_3)_4$, which Hückel † has used to demonstrate the results supposed to arise from free rotation in the case of dipole groups arranged in this way. Even at the high temperature used the tetrabromide remains absolutely non-polar, which is a clear contradiction of Hückel's prediction on theoretical grounds that electric moments may be expected to occur in all substances in which, according to classical stereochemistry, free rotation of individual dipole groups inclined to the C — C axis can take place. At any rate this case can only be understood if we assume the existence of a very considerable internal field, which prescribes well-defined equilibrium positions for the individual dipoles in the structure of the molecule as a whole. It is to be noted, however, that the result $\mu = 0$ must *not* be regarded as a proof that the molecule has the symmetry of a regular tetrahedron, but only as a proof that the molecule possesses one of the central symmetries admissible for molecules of the type Ca_4.* G. Wagner and Dengel, working at the *Chemisches Institut* in Würzburg, have recently investigated the crystal structure of $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ carefully by means of X-rays.† According to these experiments it is very probable that the crystal symmetry of these molecules is that of the space group C_{2h}, i.e. the symmetry of a plane rectangle.

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* K. L. Wolf (*Zeitschr. f. phys. Chemie*, B, **3**, 128 (1929) proposes to make the vector associated with the OCH_3 group &c. leave the axis of the molecule at an angle of 110°. Strictly speaking, perhaps, it would be more correct to take not the total vector of an ether but the component vector in the direction of the one aliphatic branch. The good numerical agreement in Wolf's results seems to indicate that either method of calculation will lead almost to the same result.

† W. Hückel, *Ber. d. dtsch. chem. Ges.*, **59**, 2832 (1926); *Zeitschr. f. phys. Chemie*, B, **2**, 454 (1929).

The possibility of free rotation of the individual dipoles is excluded in this case by the results obtained for the tetrabromide molecules in solution and in the form of vapour.

Thus in order to appreciate the significance of the genuine dipole moments in the other substances of type Ca_4 it is necessary to inquire to begin with whether the internal field is not likely to be much smaller in their case. The reasons adduced in favour of this view are scarcely convincing. As regards the dipole field, the individual group moments e.g. in $C(OCH_3)_4$ are approximately of the same magnitude, and the distance apart of the individual groups cannot under any circumstances be much greater. Here the most pressing question on the experimental side is whether the moment varies with temperature. On account of the importance of this question it seemed advisable to attack it for the vapour of this comparatively low-boiling substance, and H. A. Stuart undertook this at our request some little time ago.‡ If μ should turn out to have a constant value in this case, there are still the two possibilities, either that the molecule is *still* in its organized state or that it is *already* in the ideally uncoupled state. Here, however, owing to the fact that

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* In this connexion see e.g. the tables given by Richter, *Naturwiss.*, **14**, 893 (1926).

† See the preliminary announcement by G. Wagner, *Naturwiss.*, 1929; for details, G. Dengel, *Dissertation*, Würzburg, 1929.

‡ See also the note in Ebert, Eisenschitz, and Hartel, *Zeitschr. f. phys. Chemie* B, **1**, 113 (1928).

μ has too small a value for an uncoupled state and owing to the previously-mentioned behaviour of the halogen compounds which are so closely related to the substance in question, the second case seems by far the more unlikely.

In this way the measurement of dipole moments becomes a means for evaluating the magnitude of internal fields, for which only indirect indications have hitherto been available.

As we mentioned above, Estermann * has found without exception that P depends in a normal way on the temperature for a large number of fairly complicated molecules containing various dipole groups which, according to the usual stereochemical point of view, are free to rotate. Here again, then, the only alternatives are those mentioned above, namely, either the organized state or the ideally uncoupled state, for in a region of transition μ would have to vary to a considerable extent. According to the particular way in which the dipoles are combined in the organized state either an increase or a decrease of μ may be associated with the uncoupling process. This question can only be cleared up for any particular substance by means of a many-sided investigation; as things are at present it must in most cases still be regarded as open, for only in certain special cases is it possible to decide the matter one way or other with any degree of certainty.

V. We have still to discuss the idea which forms the basis of applications of *geometrical stereochemistry*. Classical stereochemistry —based on extensive chemical data—employs three fundamental principles to explain molecular structure, in particular the structure of aliphatic substances: (*a*) the constancy of the distances between the atoms; (*b*) the constancy of the angles between the valencies; (*c*) the possibility of free rotation. These principles express the fact that the individual parts of a molecule affect each other very little. Parts of a molecule which are at a (more or less constant) distance apart which is less than the distance between the molecules in dense gases, or of the same size as the distance between the molecules in liquids should not, especially in view of assumption (*c*), have any mutual effects sufficiently great to have a noticeable effect on the structure of the molecule. This assumption cannot be upheld from the physical point of view; for even in dense gases which are still at somewhat high reduced temperature we assume that the internal energy is considerable, while in the case of liquids the whole behaviour of the substance is characterized by the comparatively high values of the mutual forces of attraction. The structure of molecules requires that parts which are a fairly small and practically constant distance apart should even for reasons of analogy have a mutual effect on each other which is not negligible. How marked the effects of forces between molecules may be is manifested by the existence of the so-called doubly-refracting liquids or liquid crystals. Here—in contradistinction to Born's theory *—we are in general dealing not with a polar orientation of molecular dipoles with respect to one another, but with a structure depending on *apolar* orientation. Polarization along the chain, which is often considerable, was mentioned above (p. 55). Other quantitative indications of the range of forces due to intramolecular coupling may be derived from the theory of optical activity. The dimensions involved are of the order of 10^{-7} cm. according to W. Kuhn.†

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* I. Estermann, *Zeitschr. f. phys. Chemie*, B, **1**, 134, 422 (1928).

Geometrical stereochemistry provides the flexible framework which enables us to consider the many and various intramolecular fields of force which are possible. According to it the individual and hence characteristic mutual relationships of the separate parts of the molecule are expressly recognized as determining the symmetry of the whole molecule. In certain circumstances a further difficult step remains to be taken, in passing from the symmetry of the molecule as a whole (which is only obtainable by purely physical methods) to the exact determination of the position of each separate atom in the molecule. All that we can do as things are at present is to test whether the results, e.g. of dipole measurements, are in qualitative agreement with possible views of the mutual influence of individual groups. As we have already emphasized,‡ the electrostatic effect of a single dipole molecule on another similar system may vary very much according to the structure of the particular dipole. As the most natural starting-point for the discussion of the behaviour of individual groups forming part of a large molecule, we shall consider the tendency exhibited in the case of very closely related simple dipoles by the phenomenon of association. Thus from the mutual behaviour e.g. of two molecules of $CH_3 . CH_2Cl$ we infer the behaviour of two *groups* — CH_2Cl occurring in the same large molecule, or from the behaviour of the substance $C_2H_5 . OH$ we infer the behaviour of the group—$CH_2 . OH$. As a measure of the tendency towards association we take the anomalies in the dielectric or cryoscopic * properties in dilute solution, as the Ramsay-Shields method applies to the more complicated state of the pure liquid. Simple halides show a trifling degree of association, the latter being much more marked e.g. in the case of esters. From this point of view we should not expect any noticeable forces of attraction in a molecule of the type $C\alpha_4$ with four groups containing a halogen, e.g. CH_2Cl, but rather a marked repulsion owing to the (obviously negative) charges of the Cl atoms which are all similar and point outwards. According to these ideas, then, a molecule $C\alpha_4$ containing four such groups must be symmetrical about a *centre*, and this agrees with all the experimental evidence.

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* L. Ebert and H. von Hartel, *Physik. Zeitschr.*, **28**, 786 (1927); see also the recent papers on mesomorphic phases by H. Zocher and V. Birstein (*Zeitschr. f. phys. Chemie*).

† W. Kuhn, *Zeitschr. f. phys. Chemie*, B, **4**, 14 (and especially p. 34) (1929).

‡ *Zeitschr. f. phys. Chemie*, **113**, 11 *et seq.* (1924).

If, however, the one molecule $C\alpha_4$ contains four groups which have a tendency to become associated, various types of association may occur. On the one hand, as we have shown elsewhere (loc. cit.) for the case of single dipole molecules, association " in pairs " may occur, or, on the other hand, " chain association ".† The first type would indicate molecular configurations in which *two* of the four groups are more closely related than the others: such forms exist,‡ body-centred, face-centred, and asymmetric. The other type of association, however, can lead to an asymmetric form only, and this is the only one of all the configurations $C\alpha_4$ considered which possesses a natural moment.

In actual fact dipole molecules only occur in substances of the type $C\alpha_4$ if the individual dipole of the group α is a *compound* one, i.e. a dipole whose two poles may—even on chemical grounds—be regarded as relatively close together within the group α, e.g. OH, COOR, &c.§ Such a position is specially favourable for internal chain-like association, just as in the case of the chain association of entire molecules. Thus if we are to treat the moments obtained for substances of the type $C\alpha_4$ as definite natural moments, the moments obtained may be intelligibly deduced according to the point of view described here from the properties of the individual groups. Conversely, this very fact seems to favour the interpretation of the moments of molecules of the type $C\alpha_4$ as " natural ", as this interpretation—based on the proof of the existence of a strong internal field in $C(CH_2Cl)_4$ and its homologues—takes due account of all the material available, whereas from the point of view of the principle of free rotation the non-polar molecules $C(CH_2Cl)_4$, $C(CH_2Br)_4$, &c., with the individual dipoles inclined at an angle to the C—C line remain unexplained.

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* In view of the great interest which association phenomena in organic molecules now possess, it is a matter for regret that the numerous older cryoscopic measurements by Auwers and others are not available in a convenient form. A systematic working-up of them from the standpoint of modern ideas of molecular structure would be a valuable piece of work.

† L. Ebert, *Zeitschr. f. phys. Chemie*, **113**, 12 (1924); P. Debye, *Handbuch der Radiologie*, **6**, 634 (Leipzig, 1925).

‡ See Richter, *Naturwiss.*, **14**, 893 (1926).

§ For an interesting proposal for the decomposition of the total moments (which are alone available) of large groups, such as COOH, into separate components, see A. Eucken and L. Meyer, *Physik. Zeitschr.*, **30**, 397 (1929). In the case of aliphatic substances the question for which groups the moment is independent of the length of a neighbouring aliphatic chain is of special importance cf. K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, **2**, 39 (1929); O. Werner, *ibid.*, **4**, 371 (1929).

We have still to discuss the *magnitude* (according to present knowledge) of the deviations of the actual positions of the atoms from the positions deduced from the classical stereochemical models, i.e. we have to consider how far the admissibility of the three assumptions (*a*), (*b*), (*c*) above may be inferred from independent data.

(*a*) The assumption that the distances between the centres of gravity of the atoms in large organic molecules are nearly constant may be regarded as a sound approximation. To what extent constancy may be assumed in small molecules is shown by the values for the distance between the carbon and oxygen atoms in CO($1{\cdot}16 \,.\, 10^{-8}$ cm.)* and in CO_2($1{\cdot}02 \,.\, 10^{-8}$ cm.)†—i.e. variations of 10 per cent may occur. As is well known, the test of filling space properly has been successfully used when other criteria fail as a basis of selection in the investigation of the structure of crystal molecules. The distance between immediately adjacent molecules may therefore be regarded as a quantity which varies only slightly and which to a first approximation depends only on the nature of the two atoms concerned. Direct verifications may be expected to result from an increase in reliable experiments on crystals, from more extended knowledge of the moments of inertia of vapour molecules, and, in particular, from the application of the methods recently given by Debye ‡ for measuring the intra-atomic distances in vapour molecules by means of X-rays.

(*b*) As regards the angles between atomic linkages, we must distinguish between two questions, that of their existence and that of their particular magnitude. For organic compounds containing nitrogen or oxygen the *existence* of bends is clearly recognized in the first paper * dealing systematically with the connexion between orientation polarization and chemical structure to be an immediate consequence of the fact that both symmetrical ethers and symmetrical amines do possess dipole moments. The question of the *magnitude* of these angles for the various " central atoms " C, N, O or for various substituents could best be investigated by direct observation † of the distances between atoms which are not immediately adjacent. In the absence of such measurements we cannot e.g. decide whether the change in the values of μ in the series of symmetrical ethers (Stuart, Sänger, loc. cit.) is to be ascribed to a change in the angle between the oxygen valencies or to some other cause, such as polarization. According to an oral communication from Professor Debye relating to experiments which have just been carried out in his laboratories, a particularly interesting qualitative result has already been obtained for the most important chlorine derivatives of methane, namely that the distance between two chlorine atoms in carbon tetrachloride is $3{\cdot}3 \,.\, 10^{-8}$ cm., while on the other hand the distance between the two chlorine atoms in dichloromethane is certainly distinctly greater, its probable value being $3{\cdot}9 \,.\, 10^{-8}$ cm. If we assume that the distances between the carbon atom and a chlorine atom are the same in both molecules, and that the angle $\overset{\mathrm{C}}{\underset{\mathrm{Cl}\ \mathrm{Cl}}{\wedge}}$ is 110° in CCl_4, the angle $\overset{\mathrm{C}}{\underset{\mathrm{Cl}\ \mathrm{Cl}}{\wedge}}$ in CH_2Cl_2 would then have to be about 150°. Here perhaps we have to do with a comparatively marked spreading of the angle between the valencies, owing to two strongly negative atoms being close together. But obviously a much lower range of variation in the valency angle than $\pm 40°$ is sufficient to give the valency structure e.g. of a carbon atom any degree of symmetry we like. The result of the X-ray analysis of $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ which we mentioned above may perhaps be due to an even greater spreading of the valencies as compared with the classical ideas. The C_{2h} symmetry of the molecules in crystals of these isomorphic substances, which with certain provisos is to be regarded as the most probable, could only be satisfied by the five carbon atoms taking up mutual positions such that the central atom is at the centre and the four other carbon atoms at the corners of a rectangle. Here, of course, we are dealing with molecules in a crystal lattice, and their symmetry may differ from that of an isolated molecule of the same substance. The possibility of such a change has recently been discussed in detail by Weissenberg.* In view of the facts available a fairly considerable range of variation in the valency angle according to the special structure of the molecule must be admitted. We cannot go into the details of the problem of methane here. Analysis of the infra-red spectrum, however, indicates the existence of two moments of inertia which differ considerably in magnitude, a fact which is clearly irreconcilable with the regular tetrahedron model. Further investigation of all specially striking problems appears urgently called for. It must be emphasized, however, that any deviation, even if small in amount, of an actual valency configuration from the angles (i.e. from the symmetry) of the regular tetrahedron puts the heuristic importance of this model for chemical purposes in a different position from that associated with the ideas of classical stereochemistry.

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* Cl. Schaefer and B. Philipps, *Zeitschr. f. Phys.*, **36**, 399 (1926).

† W. Keesom and de Smedt, *Versl. Amsterdam*, **33**, 4 (1924).

‡ P. Debye, L. Bewilogua, and F. Ehrhardt, *Physik. Zeitschr.*, **30**, 84 (1929).

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* *Zeitschr. f. phys. Chemie.*, **113**, 17 *et seq.* (1924).

† E.g. by Debye's new method.

(*c*) The principle of free rotation may from the chemical point of view be based on the fact that no isomers of ethane are known which are distinguished from each other only by different orientations of one half of the molecule relative to the other.

This fact, of course, throws no light on the question whether there exists an " indifferent " relative motion of both molecules or whether for some reason or other only *one* definite configuration occurs in practice (i.e. one representing a state of equilibrium), or finally whether we must suppose that an equilibrium between several configurations is rapidly reached.

Some material is already available which is contrary to the idea that an individual group is largely indifferent to its orientation. In the halogen compounds of pentaerythritol the individual groups $\mathrm{C{-}C}^{\mathrm{H_2}}_{\mathrm{Cl}}$ can only oscillate backwards and forwards, there being no free rotation; otherwise the zero moment is inexplicable. Further, in liquids where the molecules contain *long* aliphatic chains those configurations in which the chains are extended almost in a straight line are by far the most frequent. According to the principle of free rotation each C—C bond could take up any possible orientation, so that numerous bent configurations (some of them very markedly so) might be expected to occur. Instructive data on the preponderance of the straight-chain forms may be gathered from Vorländer's monograph *Chemische Kristallographie der Flüssigkeiten* (Leipzig, 1924, p. 12). As is well known, the study of X-ray diffraction in liquids has led to similar conceptions. In these cases, then, even the forces between saturated aliphatic molecules (which are regarded as being relatively feeble) seem to be sufficient to confine the range of variation of the actually occurring orientations of the individual C—C bonds to a very considerable extent.

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* K. Weissenberg, *Zeitschr. f. phys. Chemie,* **139** (Haber volume), 562 (and especially p. 565) (1928). More details will be announced elsewhere regarding the statement that increase in molecular symmetry is unlikely to occur during crystallization, and the relationship between this statement and experimental results.

It is to be regretted that data which would enable us to find out by spectroscopic methods which motions are vibrations and which

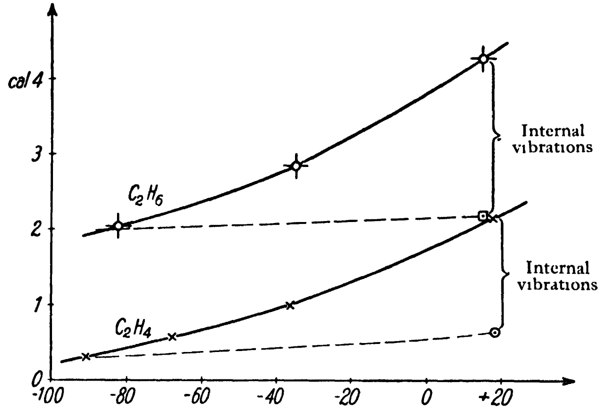

Fig. 4

are rotations are still lacking in the case of the simplest substances, C_2H_6 and C_2H_4. For this reason it is unfortunately impossible to deduce any definite information from the known molecular heats of C_2H_3 and C_2H_4, which were measured by Scheel and Heuse.* As in these cases we may expect three moments of inertia of normal magnitude, we have deducted the value $6 . R/2$ from the values of C_{v_0} and have plotted the *difference* $C_{v_0} - 3R$ against the temperature in fig. 4. C_2H_6 has a high molecular heat throughout. At the lowest temperatures the difference is 1·6 calorie, rising to 2·2 calories. In the dotted curves we have attempted to take account of the heats associated with the vibrations of the C—H and C—C bonds by calculating their values from the infra-red absorption frequencies and deducting them from the total heats. This, of course, is subject to reservations; but if we assume the validity of the correction, the state of affairs is definitely altered, as the difference now diminishes with rise of temperature. In the case of ethylene it seems natural to suppose that the slow rise of the dotted curve indicates the beginning of the excitation of the heat associated with rotation about the C—C axis. The difference of about two calories at lower temperatures may, moreover, be interpreted in more than one way; it may either be taken to mean that a torsional oscillation of one-half of the molecule relative to the other is *fully excited* in C_2H_6, or that *independent rotation* of the two halves of the molecule takes place in C_2H_6. Either phenomenon should make the same contribution to the molecular heat, namely 2 calories.

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* K. Scheel and W. Heuse, *Ann. d. Physik*, (4), **40**, 473 (1913).

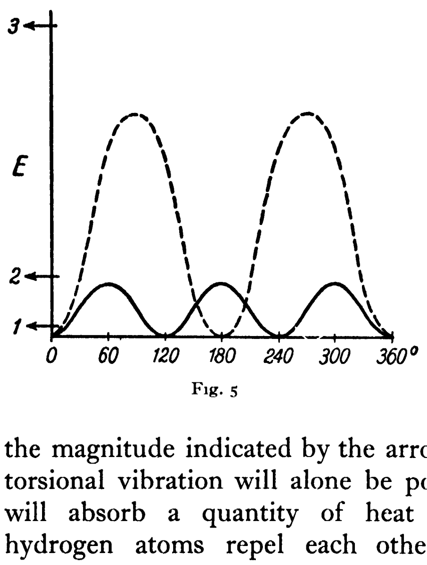

Fig. 5

The passage of a molecule from an organized state at low temperatures (with a corresponding natural moment) to an uncoupled state at high temperatures (with a different moment) may easily be understood from the case of a substituted ethane. In fig. 5 the energy of the ethane molecule is represented as a function of the azimuth ϕ (the continuous curve). If the mean kinetic energy per degree of freedom (kT) is of the magnitude indicated by the arrow 1 in the figure, a symmetrical torsional vibration will alone be possible, which—if it is excited—will absorb a quantity of heat equal to 2 calories. As the hydrogen atoms repel each other, the state of equilibrium of ethane will be the same if the two halves are rotated through 60°. If kT is larger, the vibration will pass into a spasmodic rotation (arrow 2), and finally, when kT is large, will become a practically uniform rotation, which, being the rotation of two parts of the molecule which are independent of each other, will likewise absorb 2 calories. Nothing is known about the intramolecular damping of such rotational motions. In liquid surroundings these motions will in many cases be determined by the external friction between the parts of the molecule and the solvent and in these circumstances they will acquire an aperiodic character.

The behaviour of C_2H_4 differs only as regards numerical values (see the dotted curve). The possibility of isolating *cis-trans* isomers indicates that the crest for azimuth 90° is relatively very high. Measurements of the velocity of thermal transformation for the simplest derivatives of C_2H_4 would be very desirable in order to evaluate the height of the energy crest quantitatively. In the case of more complicated derivatives (maleic and fumaric acids) experiments by Højendahl * indicate that the velocity of thermal transformation is considerable even at 150°. He obtained the value 15·8 calories for the heat of activation.

The curve of fig. 5 may be greatly altered by the introduction of large radicals into ethane, the effect chiefly depending on whether one group repels or attracts another and how great the oscillations of the curve are compared to kT.

The question whether, in the case of a large dipole molecule, we are dealing with the natural moment of the molecule as a whole or with ideally uncoupled individual dipoles forming part of the molecule can only, as we have said before, be convincingly deduced from the anomalies shown in the intermediate state. Of course no one example has been thoroughly investigated as yet. It must first be shown by experiment where the temperature range concerned comes for each substance.

In conclusion we must observe that the laws on which the actual structure of aliphatic molecules (whether isolated or in solution) depends require more accurate quantitative investigation. The heuristic importance of the usual rules for building up the molecular models of classical stereochemistry, by means of which isomers could be checked off in agreement with chemical results, is affected only in this way, that the connexion between the possible isomeric forms and the forms which actually occur must be regarded from a more general point of view. The details of the actual structure of aliphatic molecules, now available from physical methods, exhibit in many respects such marked deviations from the classical models that it is no longer possible to doubt the necessity for a more comprehensive geometrical foundation for a satisfactorily accurate description of the structure of molecules. Even in the group of compounds of type Ca_4 the agreement between the results of experiment and the requirements of classical stereochemistry is only a forced one, the principle of free rotation being partially applied and partially disowned at one and the same time. On the other hand, even with the more general geometrico-stereochemical treatment the possibility of large parts of the molecule becoming uncoupled must be

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* Kr. Højendahl, *Journ. Phys. Chem.*, 28, 758 (1924).

borne in mind; this phenomenon in certain respects resembles an intramolecular liquefaction. As yet there is no means for drawing a sharp and systematic division between the molecules in a fixed state and the molecules in a practically completely uncoupled state. A criterion would often throw light on the question whether the absolute value of the total moment for the one limiting state or for the other is the more probable. The intermediate state—representing the passage from the organized to the uncoupled state—exhibits peculiar anomalies and in doubtful cases ought to be thoroughly investigated. A reliable criterion for observed orientation polarizations would in this way enable us to draw conclusions about the presence of internal fields in large molecules and about the extent to which the structure of the latter is loosened by heat, thus once again exemplifying the fertility of the modern theory of dielectric polarization, which has already led to distinct advances in connexion with so many problems of molecular structure.

Some Theoretical Remarks on the Question of the Electric Moment and the Configuration of Molecules.

F. HUND, LEIPZIG

It may seem surprising that the theoretical discussion of molecules according to quantum mechanics has hitherto yielded no quantitative information about the dipole moment and molecular configuration. The problem, in fact, is easy to formulate but leads even in simple cases to very complicated calculations. Thus in venturing to comment on the matters under discussion from the point of view of a theoretical physicist I must in the first instance confine myself to recalling the rough qualitative ideas which have long been familiar. In connexion with these I shall touch on a point where the new quantum mechanics has caused us to change our ideas on molecular configuration.

From the rough qualitative point of view the properties of a number of molecules may be explained by the idea that they consist of *ions*. As experiments show that the molecules resist change of their distances apart to a considerable extent, it is sufficient to introduce forces of repulsion decreasing rapidly with the distance in addition to the Coulomb forces due to the charges, or simply to regard the ions as rigid spheres. The limits within which this crude idea is permissible have been considerably extended by taking the polarization of the ions into account (as was first done qualitatively by Born and Heisenberg) by assuming that the electric field $\mathbf{E}$ induces a dipole $\alpha\mathbf{E}$. Thus according to this idea of rigid ions an ion has only three properties: the charge Z, the radius R, and the polarizability α. α measures the extent to which the electrons can be displaced within the ion: if the ion is a metal sphere $\alpha = R^3$; if it is a sphere of dielectric, $\alpha = \frac{\epsilon - 1}{\epsilon + 2} R^3$.

This simple idea may within certain limits be applied to molecules whose constituents differ considerably from free ions. A number of atoms (F, Cl, Br, I, O, S, &c.) have the property of attracting electrons belonging to other parts of the molecule when they enter the latter. They make the molecules into polar molecules, and the relationships between the forces in the complete molecule qualitatively resemble those for a configuration consisting of ions.

If we pass from light ions to heavy ions the polarizability * increases more rapidly than R^3; the value of α is about 7–8 times as great for I^- as for F^-, while the volumes are approximately in the ratio of 1 : 5.

This explains the well-known fact † that in molecules where the moment is due to a halogen the moment decreases as F is successively replaced by Cl, Br, and I. If α/R^3 were constant the moment would be proportional to R for dimensional reasons. Further, the decrease in the moments with the increase of size of the anion explains the tendency of molecules with a small anion (HF, H_2O) to become associated. If we ideally represent the individual molecules as spheres of radius R with a fixed moment p, the combination of two such dipoles in series gives the energy $p^2/4R^3$. Though other forces which we have neglected may prevent association taking place, it will do so all the more readily the greater p is and the less R is, i.e. for both reasons if the anion is small. A less crude idealization is obtained if we consider the individual molecules as built up of spherical ions and investigate the equilibrium configuration and energy of groups of molecules. Here again association is favoured by a large dipole along with small dimensions.

The idea of polarizable ions also explains the shape of certain simple molecules.‡ If we ideally picture the H_2O molecule as an O^{--}-ion with two H-nuclei, no dipole is induced in the O-ion if the H-nuclei are on opposite sides of the O-ion and in such a position that the centres of the three ions lie in a straight line. If an angle is formed, however, a dipole is always produced in the O-ion; thus if the O-ion has a sufficiently high value of α the equilibrium configuration is always a bent one. The pyramidal form of NH_3 may be explained by similar considerations. This conception is too

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* K. Fajans and G. Joos, *Zeitschr. f. Physik*, **23**, 1 (1924); M. Born and W. Heisenberg, *Zeitschr. f. Physik*, **23**, 388 (1924).

† In this connexion see L. Ebert, *Zeitschr. f. phys. Chemie*, **114**, 430 (1925).

‡ F. Hund, *Zeitschr. f. Physik*, **31**, 81, and **32**, 1 (1925); *Phys. Zeitschr.*, **26**, 682 (1925).

crude for a quantitative determination of the angle between the valencies of O and N. Recent spectroscopic work * on NH_3 shows that NH_3 is a flattened pyramid (fig. 1). In molecules where the ion occurring only once is slightly polarizable and the ion occurring several times is more strongly polarizable, the ideal representation by means of ions gives the most regular configuration as that of equilibrium. CO_2 becomes a bar and the CO_3 ion an equilateral triangle with C in the middle. The configuration of CH_4 cannot be theoretically predicted in a corresponding way, as the CH bond exhibits only slight polarity. A form consisting of C^{----} with sufficiently great polarizability and four H^+ ions would give a square pyramid with the C at the vertex,† whereas a configuration consisting of C^{4+} and four H^- ions would give a regular tetrahedron with the C at the centre of gravity. The only configuration compatible with zero electric moment in this case and in the associated transitional cases is the regular tetrahedron with C at the centre of gravity. If we take induced quadrupole moments into account other forms without electric moments are possible, e.g. that shown in fig. 2 (the centres of gravity of the H-atoms are four of the eight corners of a prism on a square base with C in the centre; the prism may also be broader than it is high). The infra-red spectrum of CH_4 does not seem compatible with the regular tetrahedron configuration.‡

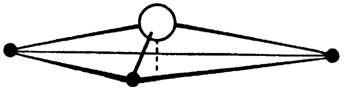

Fig. 1.—Configuration of NH_3

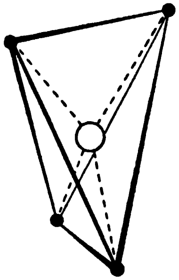

Fig. 2.—Possible Configuration of CH_4

In theory the new quantum mechanics enables us to calculate all the properties of a configuration which consists of a given number of electrons and a given number of nuclei with given charges. Owing to the correspondence between the properties of quantum and classical systems the rough representations mentioned above still hold good to a great extent. Of course the problem of deducing the empirical hypothesis mentioned above, namely that certain mole-

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* E. F. Barker, *Phys. Rev.*, **33**, 684 (1929); see also R. M. Badger and C. H. Cartwright, *Phys. Rev.*, **33**, 692 (1929).

† V. Guillemin, *Ann. d. Physik*, **81**, 173 (1926); A. E. van Arkel and J. H. De Boer, *Physica*, **7**, 354 (1927). ‡ *Ibid.*

cules become polar, F, Cl, Br, I, O, S becoming negative poles, by calculation is one for treatment by quantum methods. So far this calculation has not been carried out.

At one point connected with our problems the new quantum mechanics has led to a qualitative alteration of our ideas. In the case of *molecules with more than three nuclei*, which in equilibrium do not lie in one plane, the potential energy associated with the vibrations has two minima of equal depth. Thus a variety of conditions and frequencies arise which differ from those which the classical properties would in the first instance lead us to expect.* A simple analogy, which, however, exhibits the essential facts, is the motion of a single particle in a straight line with a potential energy $U(x)$ which is an even function of x with two equal minima (fig. 3). In the classical case, provided the total energy is less than the maximum of the potential between the two positions of equilibrium, the motion is confined to the neighbourhood either of the left-hand position of equilibrium or of the right-hand one, whereas in the quantum mechanics case a particle originally placed in the left-hand region may some time later be found in the right-hand region. The probability of the latter occurring is very small when the maximum of the potential is very large.

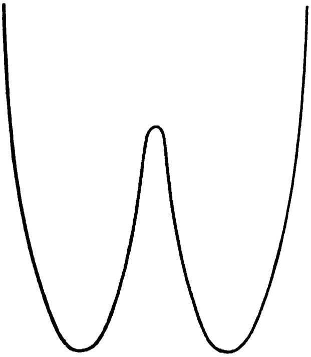

Fig. 3

NH_3 is an example of a molecule which has two positions of equilibrium with the same energy. The large variety of frequencies resulting from the quantum theory seem to be experimentally established.† Other examples are molecules in which a C-atom is attached to four different atoms or radicals. The existence of optical isomers at first seems to contradict the fact that a quantum state is always a mixture of motions in the neighbourhood of one or other of the equilibrium configurations—dextro- and lævo-configurations—and that every dextro-configuration must some time pass into a lævo-configuration. An estimation of the mean duration of a dextro- or lævo-configuration under plausible assumptions gives times which depend to a great extent on these assumptions and which may lie between times of the order of the period of vibration of the molecule and of the order of a geological period. This passage from the dextro-configuration to the lævo-configuration and the resulting racemization take place even at the absolute zero of temperature. We may expect cases to occur in which optical isomers are possible according to the structural formula but cannot be produced no matter how low the temperature. The behaviour of NH_3 suggests that the velocity of racemization in compounds of the type NABC is extremely rapid (of infra-red frequency).

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* F. Hund, *Zeitschr. f. Physik*, **40**, 742 and **43**, 805 (1927). The classical values of the vibrations for the systems exhibiting the most important cases of symmetry will be found in C. J. Brester, *Kristallsymmetrie und Reststrahlen* (Diss., Utrecht, 1923).

† E. F. Barker, *Phys. Rev.*, **33**, 684 (1929).

Similar behaviour may be expected to occur in cases where a molecule has two or more equilibrium configurations of nearly the same energy. It may happen that isomers which are possible from a geometrical point of view have only very short " lives " even when the temperature is low.

The Dipole Moment and the Velocity of Reaction

W. HÜCKEL, FREIBURG IM BREISGAU

Consideration of a simple limiting case suggests that under certain conditions easily recognizable relationships may exist between dipole moments and velocities of reaction. A molecule consisting of two rigid ions is a model dipole. In all reactions into which the molecule does not enter as a whole but which consist of ionic interchanges the molecule must first be ionized, the energy of ionization being thereby used up. Thus if the completed ions react further practically instantaneously the velocity of such reactions depends on the frequency of ionization (k) which is given by the energy of activation (q_ι): $k \sim e^{q_\iota\ RT}$. If we assume that originally there are no excited ions present, q_ι is the energy of ionization, which is equal to e^2/r for ions with a charge e at a distance r apart, or, in a solvent with dielectric constant K, equal to e^2/Kr. The stronger the charge on the ions and the smaller the distance between them the less frequent is the ionization.

Experiment suggests that these ideas which hold for strictly heteropolar compounds should also be applied to homopolar compounds whose dipolar character indicates that they are capable of becoming ionized. At a time when it was believed that hydrogen compounds could be treated as strictly heteropolar Kossel * unconsciously carried out this experiment in his interpretation of the strengths of acids. Kossel regards the dissociation constant as a measure of the frequency of ionization —how far this is permissible will be discussed later—and obtains the following result, which in many cases is in qualitative agreement with experiment: the stronger the charge on the ions and the smaller the distance between them, the smaller is the degree of dissociation. Thus for equally charged

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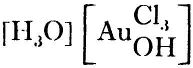
* *Ann. d. Physik*, **49**, 229 (1916).

pairs of ions the strength of the acid runs parallel with the dipole moment. Kossel's ideas find an application in the comparison of complex compounds with compounds containing elementary ions only. Thus for example the addition of SiF_4 makes the weak hydrofluoric acid H_2F_2 into the strong hydrofluosilicic acid $H_2(SiF_6)$ (or more correctly $[H_3O]_2\ [SiF_6]$, as the acid cannot be completely freed from water), and the addition of $AuCl_3$ makes the weak H_2O into the strong acid  $[H_3O]\left[Au{Cl_3 \atop OH}\right]$. But, as Kossel himself emphasized, when complex compounds are formed the readiness to undergo ionization is not only affected by the greater distance between the positive and negative charges but also by the stability of the complex ions, which in its turn depends on the size and charge of the central atom, (which Kossel regards as an ion). As the subsequent investigations of Fajans * on the molecular refraction of complex ions have shown, the layers of electrons of the outer atoms in complex ions are less readily distorted than they are when the same atoms appear as independent ions, i.e. in other words complex compounds are more strongly heteropolar than first order compounds. A second important factor which must be considered in addition to the distance between the charged atoms is the strength of the electronic bond in the individual ions as determining the ionization potential. If we take this second factor into account we simultaneously make the transition from the limiting case of rigid ions to that of homopolar dipole molecules.

Both factors affect the formation of complex compounds: an increase in the distance between the ions and a decrease in their capacity for being distorted both decrease the ionization potential. Thus, as Meerwein † has shown, Kossel's ideas suggest that in the case of many reactions depending primarily on the formation of ions, the formation of complexes will lead to a considerable rise in the velocity of reaction. The effects of different solvents which we are led to anticipate from their dielectric constants are also confirmed by experiment, in their broad outlines at least.

We shall summarize some of the observations from which Meerwein ‡ draws his conclusions. The reactions considered are the

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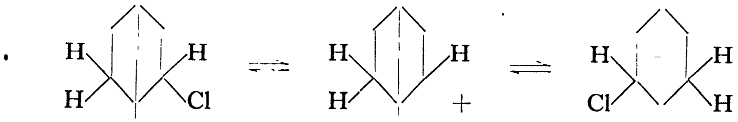
* *Naturwiss.*, **11**, 165 (1923).

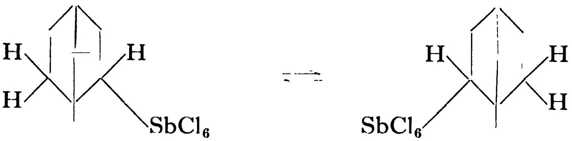
† *Ann. d. Chemie*, **455**, 227 (1927); *Ber. d. dtsch. chem. Ges.*, **61**, 1840, note 3 (1928).

‡ Meerwein and van Emster, *Ber. d. dtsch. chem. Ges.*, **53**, 1815 (1920); **55**, 2500 (1922); Meerwein and Montfort, *Ann. d. Chemie*, **435**, 207 (1924).

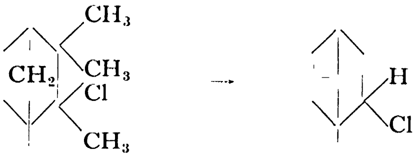
racemization of isobornyl chloride, in which ionization and subsequent wandering of the chlorine atom take place,



which is much slower than



(the distances between the atoms being indicated by the lengths of the dashes), and the transformation of camphene hydrochloride into isobornyl chloride,

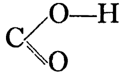


Effect of the Solvent

Velocity of Transformation of Camphene Hydrochloride

	k.	Dielectric Constant.
	At 20°	
Nitromethane	0·378	40·4
Acetonitrile	0·124	36·4
Nitrobenzene	0·0397	34·0
Benzonitrile	0·0396	26·0
	At 40°	
Anisole	0·0247	4·35
Bromobenzene	0·0184	9·82
Ethyl bromide	0·0149	9·70
Chlorobenzene	0·0123	5·57
Benzene	0·00396	2·25
Petroleum ether	0·000617	1·80
Ether	very small	4·63

The next step is to apply the ideas developed in connexion with ionization phenomena in more or less polar compounds to phenomena in which no primary ionization takes place. We shall then have to deal not with the passage of a substance into another with a greater distance between the more or less strongly distorted ions, but with a change in the dipole moment of a compound owing to the inductive effect of intramolecular electric fields or to association with another dipole. Meerwein has begun to investigate some reactions from this point of view and his experiments support these ideas to some extent, but the work is not yet sufficiently advanced to be dealt with in detail here.

The train of ideas which we have outlined above shows how we have been led to seek for relationships between the dipole moment and the velocity of reaction. At the same time, however, it indicates a limit beyond which the search cannot be expected to yield any simple relationships. For whenever we compare compounds in which the layers of electrons which form the bond between the polar groups under comparison and the rest of the molecule vary greatly in strength, it will no longer be permissible to expect that increasing the distance between the centres of gravity of the positive and negative charges will correspond to a smaller energy of activation. Hence in the first instance we can only compare compounds in which the polar groups which are joined together have electronic bonds of equal strength in each case, e.g. we may compare the O—H of  $C\begin{smallmatrix}\nearrow O-H\\ \searrow O\end{smallmatrix}$ for any carboxylic acid, but we may not compare it

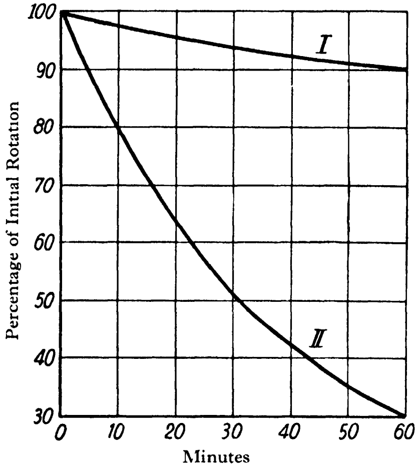
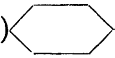
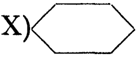
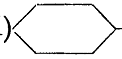


Fig. 1

with aromatic C—O—H in phenols; aliphatic C—Cl linkages may be compared among themselves, but not with aromatic C—Cl linkages (the latter also being comparable only among themselves) or with aliphatic C—I linkages.

The question also arises how far the comparison may be extended to reactions which are not ionic. In the first instance we can only say that reactions must at least exist which are related to the polar nature of the linkage, e.g. the hydrolysis of halogen compounds or esters, but not (as one might expect) the reduction of halogen compounds with hydrogen.

We now give some simple examples to show how the principle of comparison may *not* be used. The fact that the dipole moment and the velocity of reaction do not run parallel when the bonds between the atoms vary in distortability is shown in the hydrolysis of the halogen compounds CH_3Cl, CH_3Br, CH_3I; the velocity of reaction (like the velocity of reaction with $AgNO_3$ or with metals) increases in the order given, whereas the dipole moment decreases (1·89 for CH_3Cl, 1·82 for CH_3Br, 1·66 for CH_3I). Thus although e.g. in methyl iodide the electrons are further removed from the centre of gravity of the iodine atom than they are from that of the chlorine atom in methyl chloride, the former compound is more reactive and more readily forms iodine ions, because the C—I bond is more readily affected than the C—Cl bond owing to the greater weakness of the binding electrons (which we infer from a comparison of the molecular refractions).

The inadmissibility of using any arbitrary reaction as a basis of comparison follows from the fact that in certain circumstances one and the same series of compounds may exhibit exactly opposite trends of the velocity of reaction with differing reagents. Thus, for example, those benzyl bromides substituted in the nucleus, (X)—CH_2Br, which are difficult to hydrolyse to (X)—CH_2OH, are readily reduced to (X)—CH_3 by zinc and glacial acetic acid, and vice versa.

Finally, there is the general question how far the velocity constant of a reaction (k) depends on the energy of activation, for only where it does so may we expect to find a relationship between it and the dipole moment. Now by the approximate formula* $k = \alpha e^{-q/RT}$

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* *Ber. d. dtsch. chem. Ges.*, **61**, 1517 (1928).

the velocity of reaction depends, apart from the energy of activation, on the factor α, the so-called action constant, which likewise depends on the chemical constitution. It is therefore not enough merely to compare the experimental values of k (as is frequently done), but the effects of q and α must be distinguished. Unfortunately this is seldom possible, as the temperature coefficients required for the calculation of q and α are only known for one or two reactions.

We may therefore summarize the situation by saying that the search for a relationship between the energy of activation and the dipole moment seems justified for ionization phenomena in dipole molecules as well as for reactions between heteropolar compounds or definite dipole molecules or ions, it being assumed that we are dealing with reactions of polar bonds of about the same " distortability ".

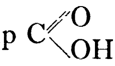
Various difficulties are met with in the attempt to verify the anticipated relationships directly. To begin with, the energy of activation, as we have already mentioned, is known only for a few reactions, and the measurement of the dipole moment itself has only been carried out for a few compounds suited to the investigation of this problem. Besides this, the moment corresponding to a linkage cannot be measured by itself, but only the moment of a molecule, and if there are several bonds of a polar nature the conclusions drawn from measurements of the total moment may in certain circumstances be unsatisfactory. For these reasons the verification of the relationships predicted can, broadly speaking, only be carried out indirectly at present.

This can be done in two ways. We may consider what effect certain substituents may be expected to have on the dipole moment of a particular bond and find whether the energy of activation is diminished to correspond with the expected increase in the dipole moment (which cannot be measured directly), and conversely. Or we may infer definite degrees of polarity of the bonds from the energies of activation and find whether these degrees of polarity are consistent with the moments calculated by combining suitable moments found by actual measurement.

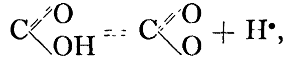
The first method is practicable when we are merely concerned with an effect (due to an electrostatic field) of distant substituents on the moment of a definite bond. This influence is manifested by the electrons of the polar bond becoming displaced, the displacement leading either to an increase or to a decrease in the original moment. Thus an induced dipole is superposed on that originally existing, either strengthening or weakening the latter. (To a first approximation a displacement of the screened atomic nucleus may be neglected.)

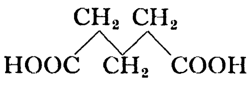
Distortion due to an electrostatic field within the molecule may arise from the presence of free electric charges, e.g. in the anions of acid esters or in the singly-charged anions of dicarboxylic acids, or from the effect of one dipole field upon another. Only in exceptional cases will the fields of non-polar parts of the molecules affect the moment of a dipole by displacing electrons, so that they may be neglected here; where they make themselves noticeable, their effect is essentially different and consists in a " screening " of the dipole field.

A free negative charge will repel the electrons. If the free end of the dipole which is transformed in the reactions and appears as an ion in the products of reaction is positive, the electrons are displaced towards this free end, the dipole is weakened, and an increased energy of activation is required to split off the positive constituent; if the free end is negative, the constituent which forms the negative ion is more readily split off.

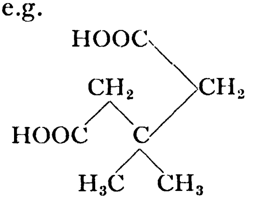
The effect of a dipole may vary according to its position; this is particularly noticeable when it occupies a special position very close to a dipole capable of reacting (e.g. in the *ortho*-position in the benzene nucleus). The two similarly-charged ends may come together; then the fields do not balance each other and the energy of activation may be expected to be smaller: or the oppositely-charged ends may come together; then the fields balance each other and the energy of activation is increased. In addition to this, however, the introduction of a polar group causes a further change in the molecule, namely, a displacement of electrons, which is propagated along the chain of atoms to the negative end of the dipole *giving rise to the distortion.* If the free end of the *reacting* dipole is negative, as e.g. in a C—Cl bond, the moment is decreased by the electrons of the chlorine atom being attracted away, and the energy of activation is increased, while if the free end is positive, as e.g. in the carboxyl group  $\mathrm{C}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\backslash\mathrm{OH}}$, the moment of the reacting O—H bond appears to be increased and the energy of activation decreased.

Extensive experimental material for testing the anticipated effects is to be found in the dissociation constants of organic acids. It must be observed, however, that the dissociation constant as a constant of equilibrium is only to be regarded as a measure of the frequency of ionization if we may assume that the opposite process of association occurs equally frequently in all cases, independently of the chemical constitution. The numerous relationships which have been obtained between dissociation constants and constitution would seem to indicate that this assumption is approximately true in many cases at least.

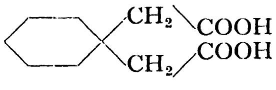
The effect of a negative charge on the energy of activation of the reaction  $C\begin{smallmatrix}{/\!/}O\\ \diagdown OH\end{smallmatrix} \rightleftharpoons C\begin{smallmatrix}{/\!/}O\\ \diagdown O\end{smallmatrix} + H^{\bullet}$, however, does not merely consist in a distortion of the carboxyl group in such a way as to make the splitting off of H• more difficult, but also results in the H•-nucleus being retained in the electric field. The latter effect may be calculated, according to Bjerrum,[*] if the distance between the negative charge and the carboxyl group is known. In the anions of polybasic acids whose carboxyl groups are very close together, the increase in the energy of activation is much greater, according to Bjerrum, than one would expect from the distance between them in the atomic model (and conversely, the distances calculated from the ratio k_1/k_2, which gives the difference in the energy of activation, are much too small). Bjerrum ascribes this to an effect acting along the chain and takes no account of the direct effect of an electrostatic field on the moment of the carboxyl group. That the latter may, however, be the essential effect follows from the subsequent experiments of Gane and Ingold [†] on substituted glutaric acids, in which the ends of the chain are brought very near each other owing to the chain being bent by the substitution of electrically neutral alkyl groups for hydrogen, e.g.



Glutaric acid.



ββ′-dimethyl glutaric acid.



Cyclohexane-1, 1′-diacetic acid.

k_1	$4{\cdot}6 \,.\, 10^{-5}$ (formerly 4·7)	$2{\cdot}0 \,.\, 10^{-4}$	$3{\cdot}4 \,.\, 10^{-4}$
k_2	$5{\cdot}3 \,.\, 10^{-6}$ (formerly 2·9)	$5{\cdot}5 \,.\, 10^{-7}$	$1{\cdot}0 \,.\, 10^{-7}$
r	9·2 (Bjerrum 5·3)	r 1·57	r 1·04

Here again we obtain impossibly low values for the distance between the carboxyl groups if we merely take account of the effect calculated by Bjerrum; but no appreciable chain effect exists in the glutaric acids. (Another possible explanation would be that the dielectric constant of water used by Bjerrum is no longer valid when the carboxyl groups are too close together.)

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[*] *Zeitschr. f. phys. Chemie*, **106**, 219 (1923).

[†] *Journ. Chem. Soc.*, 1928, pp. 1594, 2267.

The increasing of the moment of the carboxyl group by a dipole owing to the removal of electrons, which is outwardly manifested by the acid becoming stronger, has already been explained in a similar way by Ostwald and may therefore be discussed quite briefly here. The question whether the so-called negativing substituents only affect the moment by their action along the chain or by means of their field as well is not yet settled. Here we may content ourselves with the remark that in the glutaric acid series the increase in the first dissociation constant owing to the carboxyl groups in the γ-position in cyclohexane-diacetic acid approaching one another is three times the effect of a carboxyl group in the β-position in succinic acid; this at least seems to suggest that in certain circumstances the electrostatic field due to the dipole may have a considerable distorting effect.

All these examples of the electrolytic dissociation of organic acids, however, are unsatisfactory in so far as in their case there is no possibility of measuring the energies of activation of the ionization phenomena directly but only of inferring their gradation indirectly from equilibrium constants, subject to certain provisos. The energy of activation is, however, known for some cases of hydrolysis of organic halogen compounds, though no measurements are available at all for the simple halides of the aliphatic series. Thus e.g. we cannot tell whether the rapidity of hydrolysis of tertiary halogen compounds is to be ascribed to a particularly large dipole moment or not. On the other hand, the effect of substitution in the benzene nucleus on the energy of activation in the case of the hydrolysis of benzyl chloride has been thoroughly investigated by Olivier.* All substitutions which bring a second dipole into the molecule raise the energy of activation—and, as may be expected, lower the moment of the C—Cl bond which is hydrolysed, the effect being opposite to that in the ionization of the hydrogen of the carboxyl group. The introduction of the methyl group, however, makes practically no change in the energy of activation; the very considerable effect of the methyl group on the action constants has nothing to do with the moment of the C—Cl bond.

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* *Rec. Trav. Chim. Pays-Bas*, **41**, 301, 696 (1922); **42**, 516, 775 (1923).

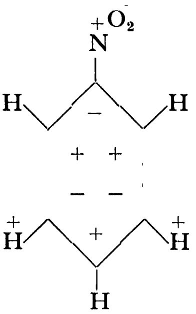
	$k_{83} . 10^3$	$k_{30} . 10^5$	q	$\alpha/10^{10}$
Benzyl chloride ..	15·5	11·1	19,950	2·9
o-CH_3	75	55	19,850	9·3
m-CH_3	21·6	14·4	20,200	5·6
p-CH_3	164	104	20,500	67
o-Cl	5·5	—	—	—
m-Cl	3·68	1·52	22,200	16
p-Cl	9·6	5·2	21,100	8·5
o-Br	4·44	2·36	21,150	4·5
m-Br	3·34	1·47	21,900	9·6
p-Br	7·8	4·57	20,850	5·1
o-I	4·45	2·48	20,960	3·4
m-I	3·11	1·52	21,500	5·0
p-I	7·4	4·14	20,950	5·5
o-NO_2	1·30	0·52	22,300	6·6
m-NO_2	1·40	0·63	21,800	3·7
p-NO_2	1·15	0·491	22,050	4·1
o-COOH	—	—	—	—
m-COOH	3·79	1·89	21,400	5·5
p-COOH	2·56	1·21	21,600	5·0
oo'-Br_2	1·87	0·71	22,510	13
op-Br_2	2·89	1·09	22,540	21
mm'-Br_2	0·84	0·32	22,540	6

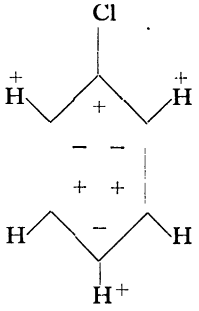
More detailed consideration of the effect of substituents in the various positions in the benzene nucleus shows a similarity between the *ortho-* and *para*-compounds as compared with the *meta*-compound. If the substituent is a halogen the energy of activation of the *ortho-* or *para*-compound is less than that of the *meta*-compound; for nitro-derivatives the reverse is true, so that it is no good trying to explain this by the different directions of the moments in *ortho-*, *meta-*, and *para*-compounds. We are dealing rather with a phenomenon which is observable in other cases, and sometimes (especially in connexion with substitutions and the reactiveness of substituents in the benzene nucleus) in a much more marked form. In cases of this type we find that when a polar group is present in the molecule the reactiveness of substituents is alternately increased and decreased in passing from one atom to its neighbour. This fact is ascribed to an alternating polarity of the linkages, and in accordance with this theory of " induced alternating polarity " it is assumed that the first polar group introduced into the molecule can confer on other bonds a polar character which changes its sign from atom to atom.

How this polar character is to be thought of is a disputed point.

The question now arises whether the dipole theory will enable us to decide between the various possible conceptions. Here, then, we have the second method of verification mentioned above, in which hypothetical values of the polarity are to be compared with actually measured moments.

We shall now briefly illustrate the ideas which have been developed about the nature of the induced alternating polarity by a few examples. The first step towards a theory was made by Vorländer, who called it the theory of electrical opposites. Vorländer * assumes that in substituted benzenes the individual atoms carry charges whose sign is determined by the nature of the substituents, e.g.:





He represents the magnitude of the electrical potential difference by the length of the strokes. That by these potential differences of the bonds he means what is now called a dipole moment follows from his notation for the salt, acid, and ester,† namely:

CH_3COO . . . . Na
CH_3COO . . . . . H
CH_3COO . . . C_2H_5.

The hydrogen atoms which have the strongest positive charges, which e.g. combine with Br_2 to form HBr or with HO—NO_2 to form H_2O, require the least energies of activation. In nitrobenzene they occupy the *meta*-position, in chlorobenzene the *ortho*- and *para*-positions.

Closely connected with this is the abnormal reactivity of certain substituents which are otherwise slow to react, which occurs when they occupy positions with a particularly large electrical opposite, e.g. chlorine in *o*- and *p*-chloronitrobenzene, but not in *m*-chloronitrobenzene.

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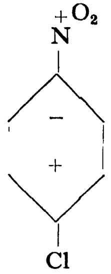
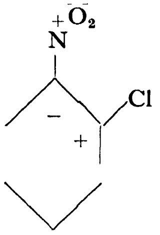
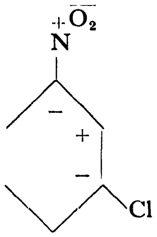
* *Ber. d. dtsch. chem. Ges.*, **37**, 1646 (1904); *ibid.*, **52**, 263 (1919).

† *Ber. d. dtsch. chem. Ges.*, **58**, 118 (1928).







Another interpretation upheld especially by Lapworth and Robinson is in conflict with Vorländer's ideas. According to it, no fixed moment is induced in the molecule by the introduction of a polar group; it only appears under the unusual circumstances occurring during the reaction.* The effect of the polar groups on the linkages in the undisturbed molecule consists rather of an alternate loosening of the electrons on the atoms marked positive and a tightening of them on those marked negative.

As yet no satisfactory theoretical foundation has been discovered for either point of view.

It should be possible to test Vorländer's theory of the induction of dipole moments, which e.g. may strengthen the polar character of the C—Cl bond (in *o*- and *p*-chloronitrobenzene) or weaken it (in the *meta*-compound) by comparing the moments of suitable compounds. If the moment of the C—Cl bond is really greater in *p*-nitrochlorobenzene than in chlorobenzene, and conversely if the chlorine causes a change in the moment of the $\mathrm{C{—}N}\genfrac{}{}{0pt}{}{=\mathrm{O}}{=\mathrm{O}}$ bonds, we cannot expect to obtain the dipole moment of *p*-nitrochlorobenzene by simple vector addition of the moments of nitrobenzene and chlorobenzene (to be subtracted in this case owing to the similarly charged ends). As according to Vorländer the *p*-hydrogen atoms in nitrobenzene and chlorobenzene are already unequally polarized by induction, measurements on the moments of these compounds do not, moreover, give the moments of the nitro-group and of chlorine in an aromatic compound, but the moments in combination with the induced moment of the C—H bond in the *para*-position (the moments of the C—H bonds in the *ortho*- and *meta*-positions cancel each other to a first approximation). Thus we shall appear to get too small a moment for the dipole group in nitrobenzene, and also in phenol, and too large a moment in chlorobenzene—if Vorländer's hypothesis is correct. In actual fact the moments of *p*-substituted compounds cannot, as one would expect, be calculated by vector addition either, unless the *p*-substituents are the same. An explanation based on the theory of induced polarities (led up to by the phenomena of the velocity of reaction) seems more probable than the assumption (discussed by Højendahl) that the *p*-substituents stand at an angle to each other, e.g.

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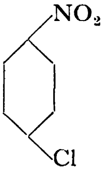
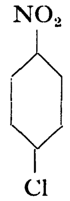
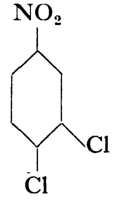
* Allan, Oxford, Robinson, and Smith, *Journ. Chem. Soc.*, 1926, p. 404, note 1.

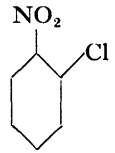


Of course, the increase of reactiveness e.g. of chlorine in *p*-nitrochlorobenzene may not merely be explained by a change of moment but may justify Robinson and Lapworth's hypothesis of the loosening of electrons on the positive atoms, which causes an increase in the dipole moment when the molecule is disturbed. For if we begin by regarding this hypothesis as fundamental, the polar group which is to cause the alternate loosening and tightening of electrons will at one and the same time, in virtue of its field, attract or repel the electrons according to its position, and in any case the electrons will be forced away from the atoms to which they are loosely attached, so that the atomic nuclei will appear positively charged as compared with their neighbours. Thus dipole moments are induced in such a way that they are readily increased still further when disturbance takes place. In this way Vorländer's hypothesis, which gives an explanation of the departures from the additive rules for the dipole moment in *p*-substituted compounds, may be combined with Lapworth and Robinson's conception of the theory of induced alternating polarities.

The effects of polar linkages within the molecule on the velocity of reaction which have been discussed hitherto are particularly noticeable in aromatic compounds (especially if unsaturated)—perhaps because the special type of linkage which occurs in the benzene nucleus is comparatively easily polarized. They include the phenomena which are usually called the "general" and "alternating" effects. In addition to these two a third effect, the so-called *ortho*-effect, has been assumed in order to explain the exceptional behaviour of many *ortho*-derivatives of benzene. In the *ortho*-position the subtituents are situated close to each other and if they are of a dipole character a considerable effect must arise from the action of the field. The fact that such an effect does arise when dipoles are close together in space is shown in the case of the dissociation constants of acids. These effects are, however, much more clearly recognizable in reactions for which the energy of activation is known. This is the case for the hydrolytic splitting off of a chlorine ion in certain polysubstituted nitrochlorobenzenes by means of sodium methylate. The values for the energies of activation (q) have been calculated from Holleman's experiments,* and the values for the action constants α, which follow from the same measurements, have been included for the sake of completeness. In each case the chlorine atom marked with a bar is removed.

		q in cal.	α (unit of time 1 minute)
1.		22·9	$2{\cdot}5 \, . \, 10^{12}$
2.		22·3	$1 \, . \, 10^{13}$

The introduction of a chlorine atom in the *ortho*-position to the *p*-Cl which is to be removed decreases the energy of activation. The C—Cl dipoles lie with the two similarly-charged ends next each other and the electric field between them is not compensated, so that the energy of activation is diminished.

		q	α
3.		23·1	$8 \, . \, 10^{11}$

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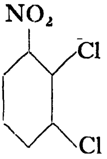
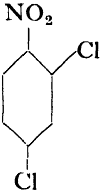
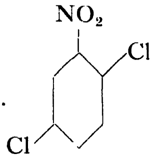
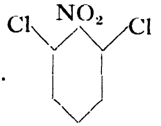
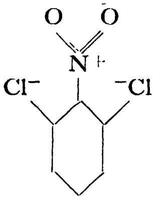
* *Rec. Trav. Chim. Pays-Bas*, **35**, 1 (1915).

		q	α
4.		23·0	$3 \cdot 10^{12}$
5.		22·7	$3{\cdot}5 \cdot 10^{13}$
6.		23·2	$1 \cdot 10^{13}$

The energies of activation are approximately equal (within the range of experimental error). The *ortho*-position in dichloronitrobenzene (4), which should exhibit a decrease in the energy of activation, is not specially marked out here. This is to be explained by the dipole of the C—Cl linkage in the middle being simultaneously " screened " on two sides; we should really have expected a decrease in the energy of activation, but this is compensated for by the screening (also referred to as *steric hindrance*). The only other effect of the second chlorine atom is to cause remarkable variations in the action constants according to its position, and hence differences in the velocity of reaction.

		q	α
7.		25·0	$4{\cdot}5 \cdot 10^{12}$

In 1-, 2-, and 6-nitrodichlorobenzene the energy of activation is much increased. As the chlorine atom removed is in a lateral position this cannot be explained as a " screening " or steric hindrance effect; if, however, we trace out the field produced by the three neighbouring dipoles accurately we obtain a perfectly symmetrical configuration, and it is easy to see that a self-compensated field of this kind due to several dipoles will require an increased amount of energy to disturb it. Hitherto all theories have failed to explain this very case.



It is probable that peculiarities in the behaviour of other compounds which contain adjacent dipoles may be capable of explanation along these lines, whereas hitherto the most that could be done to explain them has been to bring forward hazy ideas of " subsidiary valencies ".

In this paper I have attempted to indicate what connexions may be expected to exist between the dipole moment and the velocity of reaction. Our knowledge of these relationships is still, to be sure, very slight, and in this complicated region it may be that the tendencies of thought indicated here cannot all be followed out in such a way as to prove fruitful for the experimental chemist and physicist. Nevertheless it seemed to me worth while to indicate the possibilities offered by the dipole theory in that realm of organic chemistry which next to the determination of constitution is the most important, namely, the study of the relationship between chemical constitution and the velocity of reaction.

The Absorption Spectra of Di-substituted Benzene Compounds

K. L. WOLF, KARLSRUHE

In connexion with Professor Hückel's paper I propose to describe some experiments which I have begun in collaboration with Petry. These indicate the probability on other grounds that a kind of induced polarity exists in the benzene ring and by continuing them we also hope to reach conclusions about the cause of the *ortho*-effect.

The problem is briefly as follows. In calculating the dipole moments of di-substituted benzene derivatives by vectorial combination of the group moments large discrepancies between calculation and experiment are regularly obtained in the case of the *ortho*-derivatives. Attempts are made to explain these deviations either by a straining of the benzene ring (a widening of its angles), or by an electric effect on the dipole groups, which in the *ortho*-position are very near each other; in the latter case it must remain an open question whether this effect is a direct one or takes place by way of the two carbon atoms. Investigation of the ultra-violet absorption of the di-substituted products should enable us to decide on the reason or reasons actually involved.

Benzene itself of course exhibits absorption in the near ultra-violet. Substituted benzenes, such as nitrobenzene, have more extensive absorption bands in about the same region of the spectrum. Now if we compare the absorption curves of three isomeric di-substituted benzenes, we should see whether deviations occurring in the *ortho*-position manifest themselves in the benzene bands or e.g. for nitrobenzene in the nitro-band or in both.

The relationships are most clearly exhibited if we begin by choosing substances in which the substituents have no absorption bands of their own within the range of measurement. This is the case for the dichlorobenzenes. In these compounds, then, we find only the two benzene bands. Now fig. 1, in which logarithms of k, the molecular coefficient of absorption, are plotted as ordinates, shows that the introduction of a second chlorine atom into monochlorobenzene (curve I of fig. 1) causes a displacement of the bands

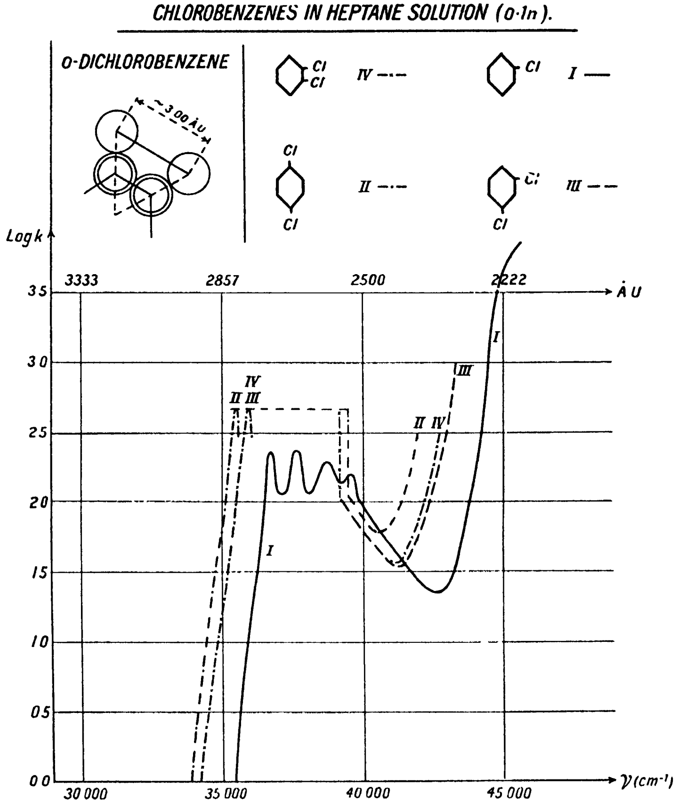


Fig. 1

as compared with those of monochlorobenzene, just as the introduction of the first chlorine atom causes a displacement of the bands as compared with those of unsubstituted benzene. What we are interested in here, however, is the relative position of the absorption bands for the three dichlorobenzenes; we see that the bands of the *ortho-* and *meta-*compounds almost exactly coincide, whereas the band of the *para-*compound is definitely displaced relative to the two others in the direction of increasing wavelength.*

If we then consider the nitrophenols and nitro-anisoles we find that they behave in an entirely different way. To begin with, the absorption band of anisole is shown in fig. 2. Here the rise of the first benzene band is as steep as in benzene itself and as in the chlorobenzenes. Thus within the range of the benzene bands the OCH_3 group (and the OH group) exhibit no absorption bands of their own. If, on the other hand, we consider the absorption curves of the nitrophenols and nitro-anisoles, we see that the curve rises much

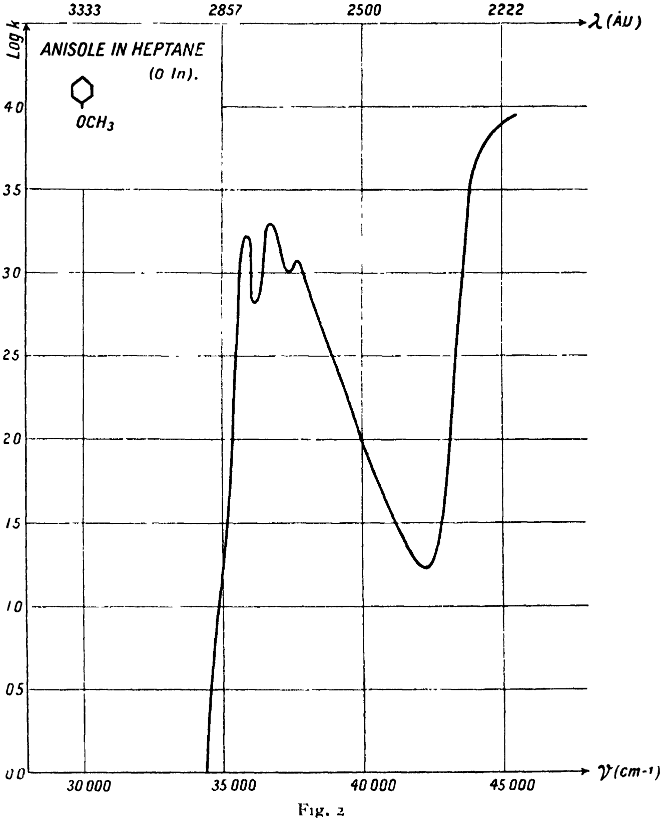


Fig. 2

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* For the sake of clearness the course of the absorption curves for the dichlorobenzenes has not been indicated between 36,000 and 39,000 cm.$^{-1}$. It is exactly the same as the curve for monochlorobenzene between 37,000 and 40,000 cm.$^{-1}$.

less steeply. This is the effect of the nitro-group, the nitro-band being superposed on the ascent of the curve. If we now compare the curves for the three nitrophenols (fig. 3), we see that the ascending parts of the curve are practically identical for the *para-* and *meta-*compounds, whereas the band for the *ortho*-compound, which coincides with that for the *meta*-compound in the case of the chlorobenzenes, is displaced in the direction of increasing wave-length.

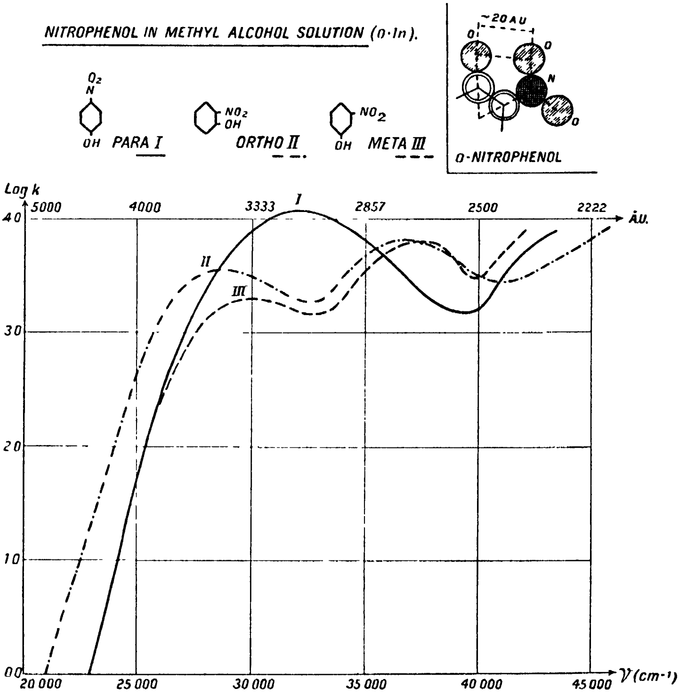

Fig. 3

The same is also true for the second band, which is definitely to be ascribed to the benzene ring. In the rest of its course, on the other hand, the absorption curve for the *para*-compound deviates entirely from the other two curves.

A detailed discussion of these relationships will be undertaken whenever the experimental material is complete. Meanwhile it is sufficient to point out that the behaviour of the absorption bands shows that other effects will be manifested in the bands besides the *ortho*-effect. It is most natural to seek for their origin in the conception of alternating induced polarities developed by Vorländer and Lapworth and Robinson, so that the absorption phenomena, apart from Hückel's work, seem to confirm the existence of this effect, although it has not yet been explained theoretically. But effects due to the solvent should also make themselves apparent, and these can only be eliminated after experiments have been carried out for a sufficient number of solvents. I would specially emphasize the point that the distances between the substituted groups in the *ortho*-position are of the same order of magnitude as the distances between the molecules or ions in concentrated solutions (see the diagrams at the top of the figures).

Molecular Associations

J. ERRERA, Brussels

In order to study molecular associations we may consider binary liquid mixtures whose constituents do not react chemically with one another and investigate the connexion between the polarity of the molecules of the components and other physico-chemical properties such as vapour pressure, viscosity, surface tension, &c.

The properties of such mixtures depend partly on the forces which occur between the elementary particles of each individual component (forces 1—1, 2—2) and partly on the forces which occur between particles of the component 1 and those of the component 2 (forces 1—2).

As Debye and Keesom have exhaustively shown, these forces are electric in nature and may result in the elementary particles becoming associated.

As we have already shown,* this molecular association may result either from permanent dipoles or from the van der Waals forces, so that we further distinguish between two kinds of molecular association:

(1) Dipolar molecular association, which must be ascribed to the electrostatic forces of the permanent dipoles in the molecule; these forces are determined by the size and position of the dipole in the molecule and the form of the molecule itself; and

(2) Non-dipolar molecular association of non-polar molecules, caused by forces of smaller range which may be related to the van der Waals forces to which the formation of homopolar molecules is due.

These two forms of association may also exist simultaneously:

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* J. Errera, *Zeitschr. f. phys. Chemie*, **138**, 332 (1928); **140**, 273 (1929).

thus we may have a total association arising from these two partial associations.

Information about this sum of the dipolar and non-dipolar associations is given e.g. by measurements of vapour pressure and viscosity, as they are functions of the " free " elementary particles Polarization experiments giving the electric moment per unit volume can only give us information about the dipolar association, as the non-dipolar association merely gives experimental effects of the second order.

In actual fact, as Debye and Ebert have shown, the total polarization consists of three parts: $P = P_E + P_A + P_P$.* $P_E + P_A$ corresponds to the polarization of those constituents whose field is determined by the van der Waals forces.

Association of the molecules makes very little difference to the value of P_E; even the association of atoms into molecules, which involves much greater forces than molecular association does, makes very little difference to the electrical polarization of the individual atoms: we know that P_E, which is often called the total molecular refraction of a molecule, is very frequently equal to the sum of the P_E's of the atoms (of the atomic refractions).

Now as P_E is ascribed to atomic electron effects it is so to speak insensitive to molecular association, and it is easy to understand that in the case of a non-polar molecule, where the total polarization is confined to $P_E + P_A$, the association cannot be measured by polarization experiments.

If, on the contrary, the molecules are polar, association of the permanent molecular dipoles makes a great difference to the value of the P_P term. This in fact is a function of the number of " free " dipoles, and association diminishes the number of these per unit volume. This explains how polarization experiments give a quantitative measure of the polar association.

This polar association may be measured by the ratio $P_{P_\infty}/P_P = y$, or as W. Ostwald † expresses it, by the ratio of the moment of inertia to the individual moment of the isolated molecule.

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* See J. Errera, *Polarisation diélectrique* (Les Presses Universitaires, Paris, 1928).

† *Kolloid-Zeitschrift*, **45**, 56 (1928).

TABLE I

Substance	P_∞	P	$P_E + P_A$	y	μ
o-$C_6H_4CH_3Cl$††	80·6	62·3	S 39·8	1·81	3·78
$C_6H_5NO_2$	348†	94	S 38·8	5·6‡	3·7
$(CH_3)_2SO_4$	282	89·3	S 54·9	6·6	3·27
m-$C_6H_4CH_3Cl$††	95	71	S 40·5	1·79	3·18
$(CH_3)_2CO$	170†	63·7‡	E 16	3·23	2·70‡
p-$C_6H_4CH_3Cl$††	105	85	S 41	1·46	2·36
p-azoxyanisole	190§	125—132	S 82	2·16	2·3
o-$C_6H_4Cl_2$	146	84·1	S 40·2	2·4	2·24
C_2H_5Br‖	103·3	55·1	A 29·5	2·9	1·86
cis-$C_2H_2Cl_2$	87	54·5	S 23	2·0	1·85
iso-amyl alcohol	86†	90·2‡	E 13	0·94	1·85†
propyl alcohol	82·7¶	65·1‡	E 17·4	—	1·76¶
$CH_2COOC_2H_5$	87†	61·7‡	E 22·2	1·64	1·74†
H_2O	64†	17·4	S 5·1	4·8	1·7
1-heptanol**	100	110·9	E 36·1	0·85	1·7
2-heptanol**	100	104·3	E 36	0·94	1·7
3-heptanol**	100	93·6	E 36	1·11	1·7
4-heptanol**	100	90	E 36	1·18	1·7
o-$C_6H_4Br_2$	102	82·2	S 43·5	1·5	1·67
CH_3COOCH_3	78†	52·3‡	E 18	1·75	1·67†
CH_3OH	63·2¶	76·8‡	E 8·1	1·9	1·64
o-$C_6H_4I_2$	105	79·3	S 49·9	1·9	1·63
C_2H_5OH	72	51·72	R 19·5‡‡	1·6	1·58
cis-C_2H_2ClBr	77·6	53·7	S 26·5	1·9	1·54
C_6H_5Cl‖	81·5	61·7	A 33·2	1·7	1·52
C_6H_5F††	69	55·3	S 28·5	1·51	1·4
m-$C_6H_4Cl_2$	79	64·2	S 39	1·6	1·37
trans-$CHCl = CHI$	62·8	50·5	E 29·4	1·5	1·27
C_6H_5I††	73	59·5	S 40	1·69	1·25
cis-$C_2H_2Br_2$	61·4	53·1	S 30	1·4	1·22
m-$C_6H_4Br_2$	73	66·9	S 42·2	1·2	1·22
$(C_2H_5)_2O$	54·9	54·9	E 23	1	1·22
$CHCl_3$‖	49·7	44·7	A 26·6	2·3	1·05
m-$C_6H_4I_2$	85	69·4	S 47·8	1·7	1·01
cis-$C_2H_2I_2$	54	50·5	S 42	1·4	0·75
cis-$CHCl = CHI$	35·2	37·0	E 28·5	0·78	0·57
o-$C_6H_4(CH_3)_2$	40·8†	42·2	E 35	0·8	0·52
$C_6H_5CH_3$	33·7†	32·7‡	E 30·3	1·42	0·4

† J. W. Williams, *Physik. Zeitschr.*, **29**, 174 (1928). ‡ W. Ostwald, loc. cit.

§ L. Ebert and H. von Hartel, *Physik. Zeitschr.*, **28**, 786 (1927).

‖ C. P. Smyth and S. O. Morgan, *Journ. Amer. Chem. Soc.*, **50**, 1547 (1928).

¶ V. D. Stranathan, *Phys. Rev.*, **31**, 664 (1928).

** Errera and Sherrill (see p. 39 of this book).

†† P. Walden and O. Werner, *Zeitschr. f. phys. Chemie*, B, **2**, 16 (1929).

‡‡ Rubens, *Sitzungsb. d. Akad. d. Wiss. z. Berlin*, 1915, p. 4.

Except where otherwise indicated the figures are by the author.

In the case of a binary mixture of liquids we know that, as Debye has shown, the total polarization $P_{1,2} = P_1C_1 + P_2C_2$, where C_1, C_2 are the molar concentrations (if, as usual, we associate the index 1 with the non-polar solvent and the index 2 with the dissolved polar substance).

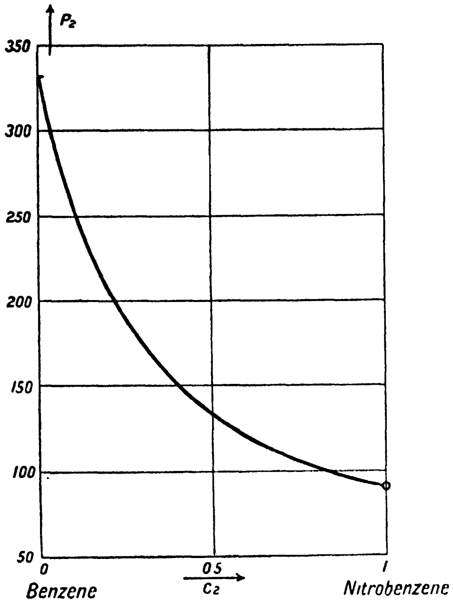

Fig. 1

The two following diagrams (figs. 1 and 2) illustrate typical ways in which P_2 may vary as a function of C_2 as described by Debye in the *Handbuch der Radiologie*. The values of the association for substances with a P_2-curve of the first type are very reliable. Some remarks on curves of the second type will be found in the earlier paper on p. 23. Table I gives some values of the association and Table II gives the change of the degree of association with concentration and temperature. We see that the dipole moment alone is not sufficient to determine the association

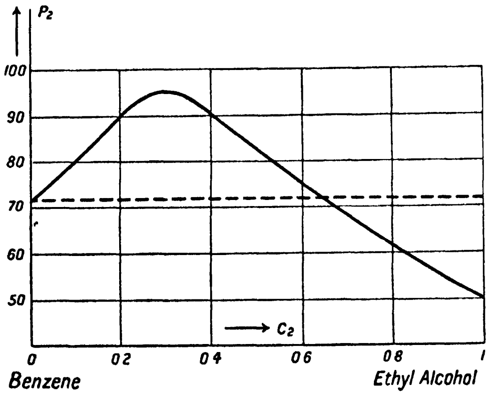

Fig. 2

and that in some cases P_{P_∞} is actually smaller than P_p. More details of these cases will be given in a subsequent paper.

TABLE II

Changes in y, the degree of association of nitrobenzene, calculated from L. Lange's experiments.* (C = concentration in percentages by weight; N = number of gram-molecules dissolved in a litre.)

C	N	P_{P_∞}	P_P	y
Temp. 24° C.				
0	0	306	306	1
3·12	0·22	306	291	1·05
6·45	0·47	306	270	1·13
11·65	0·86	306	238	1·29
29·72	2·30	306	166	1·90
100	9·83	306	61	5·02
Temp. 45° C.				
0	0	285	285	1
3·70	0·26	285	258	1·10
6·85	0·48	285	253	1·13
11·92	0·86	285	231	1·23
30·01	2·28	285	163	1·75
100	9·65	285	61·4	4·64
Temp. 65° C.				
0	0	268	268	1
4·25	0·29	268	249	1·08
7·13	0·49	268	242	1·11
12·10	0·85	268	216	1·24
31·45	2·34	268	153	1·75
100	9·52	268	62	4·32

As may be seen from the above table, we usually do not know the values of $P_E + P_A$, for which we have to carry out measurements in the remote infra-red (marked R in Table I).† We hope to be in a position to publish our first results in this region shortly. As a makeshift we may either take only the value of P_E into account (E in the table) or calculate the value of $P_E + P_A$ from dielectric constant measurements on dissolved and solid substances (S in the table) or from the temperature variation of the dielectric constant for gases or solutions (*A* in the table); but the error is greater, the smaller the value of P_P.

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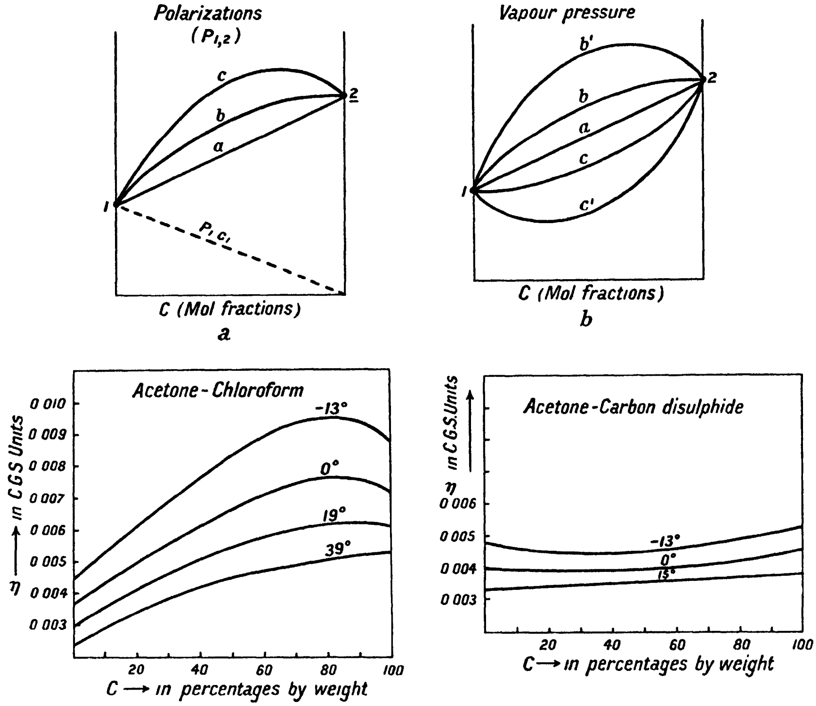
* L. Lange, *Zeitschr. f. Physik*, **33**, 169 (1925).

† The magnitude of $P_E + P_A$ must also be measured in the liquid state in order to be comparable with the other measurements. Some workers have found this value from the temperature variation of the total polarization in dilute solutions, using Debye's formula.

Taking these remarks into account, we proceed to study the experimental data on the polarization, vapour pressure, and viscosity of binary liquid mixtures. Fig. 3 shows how these quantities behave as functions of the concentration. The results may be classified in three categories:



a

b

c

Fig. 3

(1) The molecules of both media are non-polar. The variation of the polarization is represented by a straight or nearly straight line: the electrons and atoms are polarized under the influence of the applied field, but non-dipolar association, if present, only alters the magnitude of the polarization slightly. In this connexion we would remind the reader of what we have said above (p. 102).

The vapour pressure curves behave in a different way; these are either straight lines or convex curves, with or without a maximum. As we know, such a maximum results in positive azeotropism, i.e.

the boiling-point curve exhibits a minimum. These convex vapour pressure curves result from non-dipolar molecular association: diluting an associated substance with another decreases the degree of association, which increases the number of free molecules and thus explains the convexity of the curve.

The viscosity curves, apart from the linear case, are concave; in fact, if we make the molecules move further apart the forces of cohesion are diminished, which results in a decrease in the viscosity.

(2) The molecules of medium 1 are non-polar, those of medium 2 polar. In this case the polarization curves are either straight lines or convex curves. The convex curve gives us the necessary data for calculating the degree of association, starting from the idea that dilution increases the number of free dipoles and that at infinite dilution the elementary particles are free and monomolecular.

Vapour pressure experiments give results which are comparable with the polarization experiments to a greater extent than in the first case. This may readily be understood if we consider that dipolar association is due to larger forces than non-dipolar association and is registered by both methods.

The changes of the viscosity are those of case (1): the concave curve is also explained by the fact that if the molecules are further apart the forces of electrostatic attraction which caused the viscosity to rise are diminished.

(3) In the case where the molecules of both media are polar, the polarization curves give us no information, as the relationships are too complicated.

The vapour pressure curves, on the other hand, show that the curve is always concave, with or without a minimum (the existence of a minimum implies negative azeotropism) if the molecules of both components are polar or partially ionized. In this case an association of the different kinds of dipole takes place, resulting in a decrease in the free constituents; hence the decrease in the vapour pressure, which means a concave curve.

If the viscosity curve is convex, the molecules of both components are polar. This increase in viscosity may also be explained by the electrostatic forces of attraction of the dipoles, which result in an increase of the viscosity. The occurrence of a maximum in the convex curve often corresponds to the presence of a definite additive compound of the components, the existence of which may be verified by other physico-chemical methods.

Dipolar association, therefore, implies that the molecules are brought closer together by electrostatic forces, which may be compared with the forces between the ions of a crystal lattice. It occupies a position intermediate to indifference and chemical combination of the constituents. This at the same time explains the fact that even if the one constituent is non-polar the viscosity curve is nevertheless convex when a chemical compound is formed (giving rise to apparent exceptions to the preceding rule). Other exceptions to this rule may be explained by the possible occurrence of a miscibility gap between the two constituents. Before becoming completely mixed the two liquid phases pass through a colloidal state which corresponds to a maximum of viscosity.

The viscosity curves of gases dissolved in liquids confirm the rules given above.

The investigation of the temperature effect also confirms the above interpretation of the results; a rise in temperature which causes an increase in the thermal motions also causes a decrease in the convexity or concavity of the curve. Here we shall not go into the connexion between the polarity of the molecule and other physico-chemical properties such as volumetric relationships, surface tension, &c. We would merely refer the reader to papers by W. Ostwald and his pupils* in which the relationships between flocculation phenomena, changes in the degree of dispersion, swelling of gels, and polarity are discussed.

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* *Kolloid Zeitschr.* (1929).

A Simple Relationship between the Refractive Index and Dielectric Constant of Regular Crystals and the Coefficient of Repulsion in Born and Landé's Potential Equation.

K. HOJENDAHL, COPENHAGEN

A lattice of ions is distorted by an electric field in two different ways. In the first place the ions themselves are distorted. This distortion consists in a displacement of the electrons to one side and of the atomic nuclei to the other. The electrons are very light and hence can respond even to the very rapidly varying electric field of a beam of light. The shift of the electrons gives rise to refraction of light by the crystals. The second possibility is the displacement of positive ions, as such, to the one side and of negative ions to the other. The ions are heavier than the electrons, i.e. they possess greater inertia. They cannot follow the vibrations of light, and hence contribute nothing to the refraction but only to the dielectric constant. Thus by experiments on the refractive index and the dielectric constant it is possible to separate the two effects.

In order to calculate the magnitude of the second effect it is necessary to know the forces which are actually applied to the ions. If we imagine the crystal to be placed in a plate condenser and investigate the forces which act on a single ion in the lattice, these forces may be classified according to the two ways in which they arise: forces due to the charges on the condenser plates, and forces produced by the other ions. Following M. Born and A. Landé * we find it convenient to express Φ, the potential due to two ions, as the sum of two terms:

$$\Phi = -\frac{\nu\nu' e^2}{r} + \frac{\nu\nu' e^2 b}{r^q}, \quad \ldots\ldots \quad (1)$$

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* *Verh. d. dtsch. phys. Ges.*, **20**, 210 (1918).

where r is the distance between the ions, νe and $\nu' e$ are their charges, and b and q are constants. The force between the ions is obtained by differentiating:

$$f = \frac{\nu\nu' e^2}{r^2} - \frac{q\nu\nu' e^2 b}{r^{q+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The first of these terms gives the Coulomb force, i.e. a purely electrostatic force. The second term gives the repulsion between elastic spheres, such as we imagine the ions to be; hence this force is known as the elastic force. We shall first consider the electrostatic forces. In a regular lattice there are a number of ions which form a regular configuration about a central ion. A sphere with the central ion in the centre will contain such ionic configurations. It is well known that the force inside a charged sphere is zero. In the immediate neighbourhood of the centre of a regular ionic configuration the force will be very small; it is proportional to a high power of the distance from the centre. Thus the electrical forces exerted by ions within a sphere are practically equal to zero as regards the central ion. Similarly we see that the forces caused by the electronic shift are equal to zero for the ions inside the sphere. The electrostatic forces on the ion considered are therefore unchanged if we surround this ion by a hollow spherical shell. But this is how we proceed in the Clausius-Mosotti theory.* This theory leads to the following relationships:†

$$\frac{\bar{m}}{F} = \frac{3M}{4\pi\delta N}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = \gamma_E + \gamma_A \quad . \quad . \quad (3)$$

and

$$\gamma_E = \frac{3M}{4\pi\delta N}\left(\frac{n^2 - 1}{n^2 + 2}\right); \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that

$$\gamma_A = \frac{3M}{4\pi\delta N}\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right). \quad . \quad . \quad (5)$$

$\bar{m}$ is the moment induced in each molecule by the internal field F. F is the sum of all the electrostatic forces on a unit charge. The electrostatic force on an ion with charge νe is therefore $F\nu e$; M is the molecular weight, δ the density, N Avogadro's number, ϵ the dielectric constant, and n the index of refraction, so that γ_E and γ_A

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* P. Debye, *Handbuch der Radiologie*, 6, 600 (1925).

† K. Højendahl, *Studies of Dipole-Moment*, equations 14 and 18.

are the moments induced by distortion and displacement respectively by means of an internal field of 1 electrostatic unit. The displacement of the positive ions with respect to the negative corresponding to γ_A is

$$\frac{\gamma_A}{ve} = s. \qquad (6)$$

The electrostatic forces which combine to form the internal field F are balanced by the elastic forces of the last term in equation (2). If the displacement s is equal to γ_A/ve, the elastic force must therefore be ve.

In what follows only NaCl lattices with monovalent ions are considered. It is assumed that the ions are at rest (i.e. have no thermal motions) and also that the elastic forces are independent of the polarization of the ions (the electron shift).

The elastic forces decrease proportionally to a high power of the distance, so that we need only consider the nearest ions. In the NaCl lattice there are six of these, forming a regular octahedron about the central ion. For the sake of simplicity we shall only consider displacements in the principal direction (fig. 1). If ν and ν' are equal to unity, the elastic force between two ions is

$$f_2 = \frac{qe^2b}{r^{q+1}}$$

by equation (2).

The force K produced by the displacement s in the figure is

$$K = qe^2b\left[\frac{1}{(R-s)^{q+1}} - \frac{1}{(R+s)^{q+1}} - \frac{4}{(R^2+s^2)^{\frac{q+1}{2}}} \cdot \frac{s}{(R^2+s^2)^{\frac{1}{2}}}\right]$$

$$= qe^2b\left[\frac{(R+s)^{q+1}-(R-s)^{q+1}}{(R^2-s^2)^{q+1}} - \frac{4s}{(R^2+s^2)^{\frac{q+2}{2}}}\right].$$

Applying the binomial theorem and neglecting terms in s of powers higher than the first, we have

$$K = qe^2b\left[\frac{R^{q+1}+(q+1)R^q s+\ldots-R^{q+1}+(q+1)R^q s-\ldots}{R^{2q+2}} - \frac{4s}{R^{q+2}+\ldots}\right]$$

$$= qe^2b\left[\frac{2qs+2s}{R^{q+2}} - \frac{4s}{R^{q+2}}\right] = \frac{2q(q-1)e^2bs}{R^{q+2}}. \qquad (7)$$

If $s = \gamma_A/e$ this force must be equal to e (equation (6)); hence

$$e = \frac{2q(q-1)be^2\frac{\gamma_A}{e}}{R^{q+2}}$$

or

$$\gamma_A = \frac{R^{q+2}}{2q(q-1)b}. \qquad (8)$$

This formula contains two unknown constants, q and b. Another relation exists between them, which was deduced by M. Born and

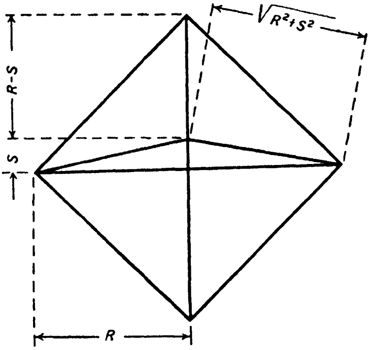

Fig. 1

A. Landé (loc. cit.). In the normal state the potential energy of the lattice must be a minimum. If we only take the six nearest ions into account in calculating the elastic forces we can deduce the following expression:

$$b = \frac{aR^{q-1}}{6q}, \qquad (9)$$

where a is Madelung's constant for an ion and R as before the least distance between two ions.

If the above value of b is included in the expression (8) for γ_A, we obtain

$$\gamma_A = \frac{6qR^{q+2}}{2q(q-1)aR^{q-1}} = \frac{3R^3}{(q-1)a}. \qquad (10)$$

If, further, the value of γ_A is introduced from equation (5), we have

$$\gamma_A = \frac{3M}{4\pi\delta N}\left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right) = \frac{3R^3}{(q-1)a}.$$

M/δ is the molecular volume, whereas R^3 is the volume which an ion occupies on the average. In the molecule there are two ions, so that NR^3 is half the molecular volume. The formula may thereby be considerably simplified:

$$\frac{4\pi}{3} N \frac{\delta}{M} \gamma_A = p_A = \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} = \frac{2\pi}{(q - 1)a},$$

or

$$q = \frac{2\pi}{a p_A} + 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

p_A as defined above is the ionic polarization. q and p_A are both pure numbers, so that the equation is formally possible. If q is infinitely great, i.e. if the ionic spheres are perfectly rigid, p_A is equal to zero. Thus in that case there is no displacement of ions. If q is equal to unity, p_A increases indefinitely. This is also illuminating, since in this case, as equation (2) shows, there is no special equilibrium distance. The equilibrium (for $b = 1$) exists for all values of r, so that the ionic spheres are infinitely distortable.

Born and Landé's equation is primarily an empirical relationship. Hence we have given some further approximations here. It is, nevertheless, interesting to compare this deduced relationship with experiment.

The result for four lattices of the NaCl type are given in the following table. Madelung's constant is 1·742. The experimental values of the refractive index are taken from the Landolt-Börnstein tables 167 and 170. The value extrapolated to zero frequency from the visible range is given in the table.

The dielectric constants are also partly taken from the Landolt-Börnstein tables (no. 194k). Average values are given in the first column of the table below. The individual values are as follows: for NaCl, Starke 6·29, W. Schmidt 5·60, Rubens and Nichols 5·18, Rubens 6·1: for KCl, Starke 4·94, W. Schmidt 4·75, Rubens and Nichols 4·55, Rubens 4·8: for KBr, R. Jaeger, 4·61, Liebisch and Rubens 5·1: for KI, R. Jaeger 5·2, Liebisch and Rubens 5·4. q is the power index which I calculated from equation (11). Dielectric constants of salts have also been determined by A. Heydweiller * (and E. Baumann). The values of $(\epsilon - 1)/(\epsilon + 2)$ calculated by Heydweiller and the values of q obtained therefrom are entered

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* *Zeitschr. f. Physik*, **3**, 308 (1920).

under the heading " Heydweiller ". q' is the power index calculated by M. Born and A. Landé * from the compressibility.

							Heydweiller		Born
	ϵ	n	$\frac{\epsilon - 1}{\epsilon + 2}$	$\frac{n^2 - 1}{n^2 + 2}$	p_A	q	$\frac{\epsilon - 1}{\epsilon + 2}$	q	q'
NaCl	5·80	1·52	0·615	0·304	0·311	12·5	0·638	11·8	7·75
KCl	4·75	1·47	0·555	0·279	0·276	14·1	0·558	13·9	9·62
KBr	4·86	1·52	0·563	0·304	0·259	14·8	0·552	15·5	9·56
KI	5·30	1·59	0·589	0·336	0·253	15·2	0·604	13·5	9·10

The indices q and q' are of the same order of magnitude, but q is about one and a half times as great as q'. The reason for this discrepancy is, of course, to be ascribed to the approximations used and also perhaps to the empirical nature of Born and Landé's equation.

Supplementary Note.

In the above we have neglected elastic forces between ions of the same kind. In particular, this is not permissible in the case where ions of the same kind touch each other. We can see the nature of the discrepancy thus caused as follows. We imagine the ions to be rigid spheres. The anions are in mutual contact, but the cations are so small that they cannot simultaneously touch all their neighbour anions. They are therefore free to move. An indefinitely small force will displace them through a finite distance. The polarization p_A due to displacement of ions or the dielectric constant therefore becomes infinite and the value of q calculated from (11) becomes equal to unity. External pressure, on the other hand, is borne by the rigid anions, so that the compressibility becomes zero and the value of q' calculated from it becomes infinitely great. The ions, of course, are not infinitely rigid, but we may nevertheless expect that in special cases like that considered above the value of q calculated from (11) will turn out considerably smaller than the value of q' calculated from compressibility measurements.

In the above table we found that q is greater than q', i.e. there are discrepancies which cannot be explained by mutual contact of ions of the same kind.

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* *Verh. d. dtsch. phys. Ges.*, **20**, 210 (1918).

The Atomic Polarization

J. ERRERA, BRUSSELS

In our previous paper (p. 101) we reminded the reader of the idea of atomic polarization.

The atomic polarization cannot be measured directly; it is equal to the difference of the polarizations $(P_E + P_A) - P_E$.

P_E is known from measurements of the refractive index in the near infra-red. These measurements must be made with a wavelength which is sufficiently far removed from the ultra-violet absorption bands and also far enough removed from the first infra-red atomic vibration. Between these two regions of absorption the curve of refractive index is S-shaped. Thus the refractive index may either be measured directly or extrapolated from measurements in the visible region.

In order to determine the values of $P_E + P_A$ we must distinguish between various cases:

A. Gaseous and liquid media.

(1) For non-polar substances the index of refraction may be measured either in the remote infra-red or in the Hertzian region.

(2) For polar substances the measurement must be made in the remote infra-red, as for short Hertzian waves the refractive index increases again as predicted by Debye's theory.

B. Solid substances. Here, as we have shown elsewhere, we have to distinguish two regions:

(1) at low frequency and in the neighbourhood of the melting-point.

(2) at high frequency and far from the melting-point. If we merely confine ourselves to this second region, we can say quite generally that for solid bodies we obtain $P_E + P_A$ only.

We investigated the values of P_A for solid, liquid, and gaseous media, but in this preliminary communication we shall confine ourselves to the solid state.

In connexion with the investigation of this region the ratio of the squares of the refractive indices (which is equal to the reciprocal ratio of the squares of the velocities of light of varying wave-length, i.e. to ϵ/n^2) is of interest as well as the polarizations. The following table gives some preliminary results calculated from experiments by Rubens.* These bodies have ionic lattices and it is natural that the atomic effects should be greatest in the ionic lattice. With reference to the work of V. M. Goldschmidt, Grimm, Fajans, Joos, and others † we may state that the two first examples are of the type AX_2 with a rutile structure. According to these and other measurements on oxides and fluorides to be published later the ratio ϵ/n^2 appears to be greater the more the quotient of the atomic radii (R_A/R_X in Table I) decreases. These results will have to be brought into relation with Bollnow's calculations on the lattice theory of rutile crystals.‡ On the other hand, the more polarizable the atoms are, the smaller does the ratio ϵ/n^2 seem to become. The polarizability depends on the displacement of the outer layer of electrons only. As an example we may mention our experiments on CdI_2 and CdF_2, which run parallel to the passage from the fluorite structure to the layer structure of cadmium iodide.

TABLE I

Atomic Polarizations

	R_A/R_X	ϵ/n^2	P_A $P - P_E$
SnO_2	0·56	$\parallel$ 24·4/12 = 5·83	19·18 — 11·05 = 8·13
		$\perp$ 23·4/3·72 = 6·3	19·12 — 10·31 = 8·81
TiO_2	0·48	$\parallel$ 167/5·8 = 28·8	18·43 — 11·52 = 6·91
		$\perp$ 83/6·5 = 76·5	18·10 — 12·12 = 5·98
NaCl	0·54	6·1/2·28 = 2·68	16·96 — 8·06 = 8·90
KCl	0·735	4·8/2·13 = 2·26	20·93 — 10·25 = 10·68
KBr	0·68	5·1/2·34 = 2·18	24·99 — 13·36 = 11·63
KI	0·605	5·4/2·62 = 2·06	31·53 — 18·6 = 12·93

In the latter cases, those of substances crystallizing in a lattice of the NaCl type in which the symmetry is much greater, no definite rule is manifested. We propose to make dielectric constant measurements for the series of substances for which Spangenberg and his pupils * have determined the refractive index.

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* Rubens, *Berl. Ber.*, 1915, p. 4; 1921, p. 11.

† For the literature see e.g. V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

‡ *Zeitschr. f. Physik*, **33**, 741 (1925).

Summarizing, we may say that in ionic lattices the ratio ϵ/n^2 is closely related to the crystal structure. The fundamental data are therefore the number, the diameter, and the polarizability of the individual constituents. Our point of view differs from that of Fajans and Joos, Grimm, Goldschmidt, &c., who are concerned with the electronic polarization (P_E), whereas this paper is intended to throw some light on the motion of the elementary constituents in the lattice (P_A).

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* *Zeitschr. f. Kristallogr.*, **57**, 494 (1923); M. Haase, *ibid.*, **65**, 509 (1927).

The Kerr Effect and Molecular Structure

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Structural problems of organic chemistry have been revived by the theory of permanent dipoles; in particular, in the case of benzene derivatives it has been possible, as a result of dipole moment experiments, to confirm and extend former conceptions in organic chemistry. In aliphatic substances, on the other hand, the relationships are usually so complicated, owing to uncertainty about the effect of the " free rotation " of groups postulated by classical stereochemistry, that it is impossible to make definite statements based on moment experiments only. I will therefore attempt to show how our goal may be reached even in very complicated cases by combining moment experiments with those on the Kerr effect and the scattering of light. It may not be superfluous to emphasize the fact that we are here dealing with matters which the rapid development of quantum mechanics has to some extent thrown into the background, but which enable us to obtain information about properties of molecules which determine their chemical behaviour, especially in cases where we cannot as yet expect any results from the quantum theory of homopolar compounds.

I now proceed to discuss the relationship between the methods I have mentioned, starting from the results of recent experiments on the electric moments of di-substituted benzene derivatives. These, in fact, have shown that in most cases it is possible to calculate the moment of the di-substituted benzenes by vectorial combination of the " group moments " of the substituents. Regular discrepancies of considerable magnitude between experiment and calculation only occur in the *ortho*-compounds and in benzene derivatives in which at least one of the substituents is an NH_2 or OH group, or else a group with a " bridge " oxygen atom, such as the OCH_3 group. In the former case these discrepancies are ascribed to mutual interference of the groups, which in the *ortho*-position are very close together, and in the latter case to the fact that in the instances concerned the "valency angle" of about 110° in the oxygen or nitrogen atom must be taken into account.

This valency angle is no new idea in organic chemistry. The essential fact is that this angle is now obtained directly for the first time by means of vector combination of the moments. Hitherto, however, it has only been possible to carry out these calculations for a few substances.[*] Hence the fact is of importance that (as I shall show by means of one or two examples) the depolarization of scattered light and the Kerr effect enable us to prove the existence of such angles and to calculate their value, even when free rotation, which gives rise to errors in the vectorial combination, is present.

We now have to introduce some notation. The Kerr constant B is defined by the relationship

$$B = \frac{K_e n_o}{\lambda} = \frac{n_p - n_s}{\lambda E^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

According to Debye's statement of the Born-Langevin-Gans theory,[†] we have

$$B = \frac{n_p - n_s}{\lambda E^2} = \frac{(n_o^2 - 1)(n_o^2 + 2)}{4 n_o \gamma_o \lambda} \left(\frac{\epsilon + 2}{3}\right)^2 (\Theta_1 + \Theta_2), \qquad (2)$$

or $B = A\Theta_1 + A\Theta_2 = B_1$ (term due to anisotropy alone)

$+ B_2$ (dipole term), ... (3)

where

$$\left.\begin{aligned} \Theta_1 &= \frac{1}{45kT}\,[(a_1 - a_2)(b_1 - b_2) \\ &\qquad + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)] \\ \Theta_2 &= \frac{1}{45k^2T^2}\,[(\mu_1^2 - \mu_2^2)(b_1 - b_2) \\ &\qquad + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)] \end{aligned}\right\} \quad . \qquad (4)$$

The quantities μ_i are the components of the permanent moment referred to a system of axes fixed in the molecule, and the quantities a_i are the components of the ellipsoid of distortion, likewise referred to axes fixed in the molecule. They define the mobility of the charges in the molecule for the case of an electrostatic field, i.e. they determine the components of the moment induced in the molecule by an electrostatic field of unit strength. The quantities b_i

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[*] K. L. Wolf, *Zeitschr. f. phys. Chem.*, B, **3**, 128 (1929); A. Eucken and L. Meyer, *Physik. Zeitschr.*, **30**, 397 (1929).

[†] P. Debye, *Handbuch der Radiologie*, **6**, (Leipzig, 1925).

define corresponding constants for the case of an alternating field and are therefore functions of λ. The system of axes fixed in the molecule is chosen in such a way as to coincide with the axes of the ellipsoid of optical polarization. Following Gans,* we may further put

$$\frac{a_i}{b_i} = \frac{\epsilon - 1}{n^2 - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5')$$

(or in dipole molecules $\frac{a_i}{b_i} = \frac{n_\infty^2 - 1}{n^2 - 1}$, where n_∞ is the index of refraction extrapolated to infinite wave-length), which is usually permissible. Then

$$\Theta_1 = \frac{1}{45kT}\left(\frac{n_\infty^2 - 1}{n^2 - 1}\right)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2], \quad (5)$$

being a sum of squares, is always positive, whereas the sign of Θ_2 still remains to be considered.

We begin by observing that a large number of molecular constants enter into the equation for the Kerr constant. In most cases, therefore, the evaluation for a typical case only offers a prospect of success if some of these constants can be obtained in another way, e.g. by moment experiments and experiments on the depolarization of scattered light. As yet, however, sufficiently accurate experiments on vapours, for which alone the theory has been developed, are still unavailable in most cases. In liquids the phenomena are interfered with by association and the uncertainty about the field actually acting on the molecule. Nevertheless we may at least apply the theory qualitatively, and the numerous experiments on liquids already serve to show that very satisfactory confirmations of the old organic structural chemistry can be obtained by combining data on the scattering of light with the Kerr constant and values of the electric moment, and that in many cases we may make further statements, especially as regards the limits to free rotation. In collaboration with Dr. Briegleb I have entered on detailed investigations of this matter. Here I can only go into the facts directly concerned with the problem of the angle mentioned above, which involves consideration of the sign of Θ_2. For the sake of simplicity, moreover, I choose cases in which the distortion ellipsoid may be taken as a surface of revolution, i.e. in which we may assume

$$b_2 = b_3 \text{ and } a_2 = a_3.$$

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* *Ann. d. Phys.*, **65**, 97 (1921).

Our formula for Θ_2 may then be simplified as follows:

$$\Theta_2 = \frac{1}{45k^2T^2}[(\mu_1^2 - \mu_2^2)(b_1 - b_2) + (\mu_3^2 - \mu_1^2)(b_2 - b_1)]. \quad (6)$$

Then if say $\mu = \mu_1$, i.e. $\mu_2 = \mu_3 = 0$, we have

$$\Theta_2 = \frac{1}{45k^2T^2}[\mu_1^2(b_1 - b_2) - \mu_1^2(b_2 - b_1)] \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

$$= \frac{1}{45k^2T^2}[2\mu_1^2(b_1 - b_2)].$$

If, further, $b_1 > b_2 = b_3$, i.e. b_1 is the axis of maximum polarizability, Θ_2 is *positive*, whereas if $b_1 < b_2 = b_3$, Θ_2 is *negative.** If μ has a medium value the angle between the direction of μ and the axis of maximum polarizability will enter into the above arguments in such a way that when the angle varies continuously Θ_2 will pass from positive values through zero to negative values.

In general † formula (6) shows that Θ_2 and hence B_2 may equally well be positive as negative for dipole molecules (and only for such). Thus the sign of Θ_2—and this is what interests us here—gives us information about the position of the moment relative to the axis of maximum polarizability.

This result never leads to ambiguity so long as B can be split up into terms B_1 and B_2. This may be done either by measuring the temperature variation of B (for Θ_1 varies as $1/T$, Θ_2 as $1/T^2$) or by calculating Θ_1 and B_1 from the anisotropy as determined by light-scattering.‡

The desired information may, however, often be obtained from the sign of B without this splitting-up process; seeing that reliable data on the scattering of light are often wanting, this is of importance.

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* Thus, pictorially speaking, negative values of B arise as a result of the great majority of the molecules setting themselves so that their moments lie in the direction of the external field. Then if the axis of *minimum* polarizability coincides with the direction of the moment, $n_p < n_s$, i.e. B is negative. If they have no fixed moment, on the other hand, the molecules preferably (at least in so far as the assumption of equation (5) is permissible) set themselves with the axis of maximum polarizability parallel to the field. Then $n_p > n_s$, i.e. B is always positive.

† In general $\Theta_2 = \frac{1}{45k^2T^2} 2\mu^2(b_1 - b_2)$ for $\mu = \mu_1$,

$$\Theta_2 = \frac{1}{45k^2T^2}[-\mu^2(b_1 - b_2)] \text{ for } \mu = \mu_2 \text{ and for } \mu = \mu_3.$$

‡ Raman and Krishnan, *Phil. Mag.* (7), 3, 713, 724 (1927); for a more exact investigation see H. A. Stuart, *Zeitschr. f. Physik*, **55**, 358 (1929).

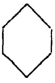
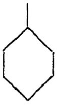
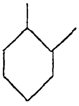
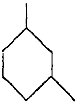
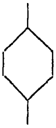
For in general, as may be seen * from the following comparison of the Kerr constants of non-polar and polar molecules (see Table I), and as is also shown by the above-mentioned decomposition of B, $|\Theta_1| < |\Theta_2|$. Even so small a moment as that of *toluene* ($0{\cdot}4 . 10^{-18}$) results in the Kerr constant being double that of the non-polar substance benzene (see Table I*a*). As experiments on the scattering of light show, the anisotropy term is to be taken as practically the same for both.§ With its relatively very large moment ($3{\cdot}9 . 10^{-18}$),

TABLE I †

Substance	$\mu . 10^{18}$	B	Substance	$\mu . 10^{18}$	B
Ethane	0	1	Ethyl chloride	about 1·9	300
Hexane	0	1·73	Methyl chloride	about 1·9	250
Benzene ..	0	12·1	Nitrobenzene	3·89	6000
p-xylene ..	0	22·6	Chlorobenzene	1·55	385
Cyclohexane ..	0	2·30	Cyclohexanol	1·7	−286
CCl_4	0	2·30	Nitromethane	3·8	330
$C(NO_2)_4$ ..	0	3·0	Paraldehyde	?	−713

TABLE I*a*

(BENZENE, TOLUENE, AND THE XYLENES)

					
B	12·1	24·3	41·2	24·4	22·6 †
$\mu . 10^{18}$	0	0·4	0·6	0·4	0
Δ_{gas} ‡	0·042	0·046	—	0·046	§

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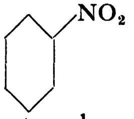
* It would be more exact to introduce the quantities $B/(\epsilon + 2)^2$. This makes the differences in Table I less abrupt, without essentially altering the results so far as we are concerned here. Here, therefore, we may dispense with the consideration of the factor $1/(\epsilon + 2)^2$, all the more so as these matters will be dealt with elsewhere in collaboration with Dr. Stuart.

† R. Leiser, *Abhandlungen der deutschen Bunsengesellschaft*, No. 4 (1910); values relative to $CS_2 = 100$.

‡ Δ_{gas} = depolarization factor of the vapour.

§ See the article by Gans in Vol. 19 of the *Handbuch der Experimentalphysik* (Leipzig, 1928); also Ramakrishna Rao, *Indian Journ. of Physics*, **2**, 61 (1927).

which, as in the case of toluene, lies in the direction of an axis of maximum polarizability, namely in the plane of the benzene ring,  has a very large Kerr constant. Thus, provided μ does not make an angle differing widely from 90° or 0° with the axes of the distortion ellipsoid, we may only expect $|\Theta_1|$ to exceed $|\Theta_2|$, i.e. $|B_1|$ to exceed $|B_2|$, in the case of very small moments.

Hence the following relationship exists between the sign of B and the position of the moment in the molecule. *If B is negative the moment in every case is (at least approximately) at right angles to an axis of maximum polarizability. On the other hand, B is not necessarily negative if μ is at right angles to such an axis, this converse statement being true only for B_2.*

If we now proceed to consider those mono- and di-substituted benzene derivatives in which as a good approximation we may assume the existence of rotational symmetry, as is shown by the values of the depolarization factor of scattered light differing only slightly from the values for benzene *, we have the following state of affairs.

TABLE II

Substance	$\mu \cdot 10^{18}$	B	Substance	$\mu \cdot 10^{18}$	B
$C_6H_5 \cdot F$	1·39	191			
$C_6H_5 \cdot Cl$	1·55	385	$C_6H_5 \cdot NH_2$	1·51	− 38
$C_6H_5 \cdot Br$	1·50	374	$C_6H_5 \cdot OCH_3$	1·2	+ 35
$C_6H_5 \cdot I$	1·25	288	$C_6H_5 \cdot O \cdot C_2H_5$	1·2	+ 40·8
o-$C_6H_4 \cdot CH_3 \cdot Cl$	1·39	270	o-$C_6H_4 \cdot Cl \cdot OH$	1·30	+ 189
p-$C_6H_4 \cdot CH_3 \cdot Cl$	1·74	711	$C_6H_3 \cdot CH_3 \cdot C_3H_7 \cdot OH$(1-4-2)	1 − 2	+ 82·6
$C_6H_5 \cdot NO_2$	3·89	6000	$C_6H_5 \cdot NH_2$	1·51	− 38
o-$C_6H_4 \cdot CH_3 \cdot NO_2$	3·75	3300	o-$C_6H_4 \cdot CH_3 \cdot NH_2$	1·5−2·0	− 73
m-$C_6H_4 \cdot CH_3 \cdot NO_2$	4·20	3400	m-$C_6H_4 \cdot CH_3 \cdot NH_2$	about 1·5	− 128
p-$C_6H_4 \cdot CH_3 \cdot NO_2$	4·50	6400			

Thus negative or small positive Kerr constants only occur in molecules with a large moment if the substituted group is an OH or NH_2 group. But since in benzene the axis of maximum polarizability lies in the plane of the ring, this means that in these two groups the moment must be inclined at a large angle to the plane of the ring. In general this is the result to which vector combination of the moments would have led in isolated suitable cases.*

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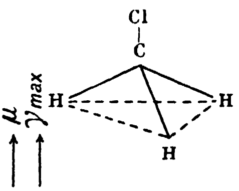
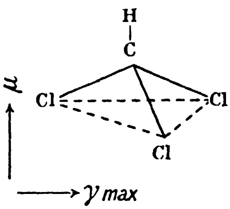
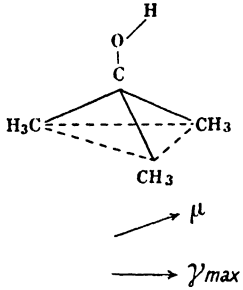
* See the article by Gans in Vol. 19 of the *Handbuch der Experimentalphysik* (Leipzig, 1928); also Ramakrishna Rao, *Indian Journ. of Physics*, **2**, 61 (1927).

† See second footnote, p. 123.

In addition to this we can now proceed with the help of the Kerr constants to prove the existence of the valency angle in the oxygen atom in aliphatic compounds also, as shown in Table III.

TABLE III

Methyl Chloride.	Chloroform.	Tertiary Butyl Alcohol.
		
$B = +250$	$B = -100$	$B = +154$
μ = about $1{\cdot}90 \,.\, 10^{-18}$	$\mu = 1{\cdot}10 \,.\, 10^{-18}$	μ = about $1{\cdot}70 \,.\, 10^{-18}$

Here, to begin with, we see two splendid verifications of our formulæ in chloroform and methyl chloride. Further, we see how the Kerr constant of tertiary butyl alcohol proves the existence of the valency angle in oxygen.†

If we consider the other aliphatic alcohols we obtain positive Kerr constants only in the cases of isopropyl alcohol and tertiary amyl alcohol, but these are much smaller (+73 and +39·8 respectively). All other alcohols with saturated chains have negative Kerr constants, which means that if there is free rotation in straight-chain alcohols the axis of maximum polarizability in general stands at right angles to μ. Calculations of angles are not as yet possible (the alcohols being liquids) but we see here how it is possible to obtain information about the mean position of the axis of maximum polarizability without detailed knowledge of the distribution of individual groups in space. In the saturated aliphatic alcohols with normal chains, in particular, the negative values for *B* suggest that in liquids long extended zig-zag chains are very frequent. This conclusion seems to be supported by a comparison of their Kerr constants with the Kerr constants and light-scattering effects of normal saturated hydrocarbons. Further, there appear to be indications that in chains with 4–5 carbon atoms with a terminal polar group the plane ring arrangement is favoured. This latter statement, however, requires further detailed investigation.

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* J. W. Williams, *Physik. Zeitschr.*, **29**, 271 (1928); K. Højendahl, *Studies of Dipole-Moment* (Copenhagen, 1928); and the papers quoted in the footnote on p. 120.

† For bromoform $B = -86{\cdot}2$, and the value for iodoform is even greater. Thus the anisotropy increases and $|\Theta_1|$ becomes greater as we pass from chloroform to iodoform. This leads to the idea that the iodine atoms originally lie more nearly in the same plane as the C atom than the chlorine atoms do, a result which agrees with other data relating to these substances.

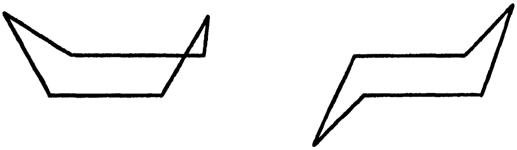

Fig. 1

In conclusion we shall discuss the case of paraldehyde, which has an unusually large negative Kerr constant (—713). How is this to be explained? In organic chemistry the two forms for cyclohexane shown above (fig. 1) are assumed to co-exist. This assumption is confirmed by the fact that cyclohexanone has the same moment as normal aliphatic ketones.* Nothing is known, to be sure, about the moment of paraldehyde. But some statements based on the given model may be made about its possible size and direction, as indicated by the two following figures (fig. 2) which are based on the assumption that the moment of each oxygen atom is similar to that in ether (the ring being unstrained).

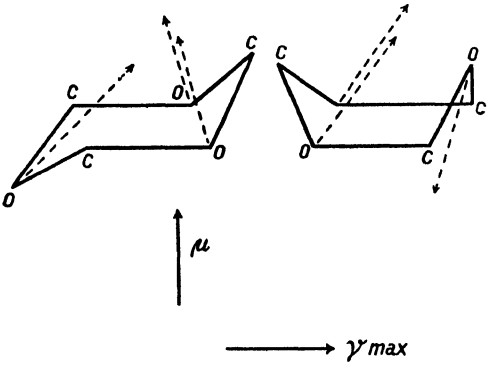

Fig. 2

We see that in both cases there results a finite moment in a direction approximately perpendicular to the direction of maximum polarizability (indicated in the figure). This explains the negative Kerr constant and at the same time yields the result that paraldehyde must have a moment of medium size at least.†

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* K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, **3**, 128 (1929); A. Eucken and L. Meyer, *Physik. Zeitschr.*, **30**, 397 (1929).

† This may indicate that the " step form " of paraldehyde occurs more frequently than the " trough form ".

In connexion with this we shall also briefly consider the relationship between the magnitudes of μ and B. To begin with, it is found that in the case of molecules in which the moment lies along the axis of maximum polarizability the magnitude of the Kerr constant almost always runs parallel with the magnitude of the moment. Hence we would specially emphasize this similarity in the behaviour of μ and B in the series of benzene halides, as it means a confirmation of the moment experiments,* which gave the surprising result that for C_6H_5Cl there is a maximum. We would further emphasize that cymene (p-$C_6H_4 . CH_3 . CH(CH_3)_2$), which has a greater anisotropy than benzene, also has a Kerr constant which is only very slightly greater (15·7 instead of 12·1). In comparison with toluene ($B = 24{\cdot}3$ for a value of μ equal to $0{\cdot}4 . 10^{-18}$) this means that cymene has a vanishingly small moment. Thus in cases where, as in the present one, a direct measurement would be very troublesome (the moment being very small) the Kerr constant may not only give information about the position of the moment but also about its magnitude. An accurate calculation of the latter is, however, only possible in combination with the values of the depolarization factor.

Summarizing the position, we may say that the present measurements of the Kerr constants for liquids provide a confirmation and extension of the results obtained by means of moment experiments. On the other hand, experiments on gases and vapours or solutions are (for the reasons mentioned at the outset) alone suitable as a basis for more far-reaching conclusions (such as the more accurate evaluation of the angle between the direction of the moment and the axis of maximum polarizability). Such experiments have already been set agoing in collaboration with Dr. H. A. Stuart. As regards the qualitative conclusions reached above, however, the uncertainty about association and the internal field need not be taken into account, as it is of course always possible to compare molecules of the same moment and of similar structure in Table II,† and, moreover, a reversal of sign owing to these factors being taken into account is unlikely to occur.

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* P. Walden and O. Werner, *Zeitschr. f. phys. Chemie*, B, **2**, 10 (1929).

† This means that only those cases are compared in which the internal field is of the same nature and in which the factor $1/(\epsilon + 2)^2$ (see first footnote, p. 123) plays a subordinate part only.

AUTHOR INDEX

Allan, 90.
Andrews, D. H., 50.
Arkel, A. E. van, 75.
Auwers, 65.

Badger, R. M., 75.
Baeyer, A. von, 35.
Barker, E. F., 75, 76.
Bewilogua, L., 66.
Birstein, V., 64.
Bjerrum, N., 55, 86, 87.
Bollnow, 116.
Born, M., 64, 73, 74, 109, 112, 113, 114, 120.
Brester, C. J., 76.
Briegleb, 121.

Cartwright, C. H., 75.
Colley, 53.

De Boer, J. H., 75.
Debye, P., 1, 2, 10, 23, 32, 39, 53, 55, 65, 66, 67, 101, 102, 103, 110, 115, 120.
Dengel, G., 62.

Ebert, L., 21, 32, 43, 45, 47, 55, 62, 64, 65, 74, 102, 103.
Ehrhardt, F., 66.
Eisenschitz, R., 21, 43, 55, 62.
Emster, van, 80.
Errera, J., 23, 25, 27, 33, 35, 39, 41, 47, 51, 101, 102, 103, 115.
Estermann, I., 15, 17, 20, 21, 27, 51, 52, 53, 58, 59, 60, 63.
Eucken, A., 65, 120, 126.

Fajans, K., 74, 80, 116, 117.

Gane, 86.
Gans, 120, 121, 123, 124.
Goldschmidt, V. M., 116, 117.
Grimm, 116, 117.
Guillemin, V., 75.
Gutton, 25.

Haase, M., 117.
Hartel, H. von, 21, 62, 64, 103.
Heisenberg, W., 73, 74.
Henne, 33.
Heuse, W., 69.
Heydweiller, 113.
Højendahl, K., 27, 30, 60, 71, 109, 110, 125.
Holleman, 92.
Hückel, W., 32, 36, 61, 62, 79, 95, 99.
Hund, F., 10, 30, 73, 74, 76.

Ingold, 86.
Isnardi, 24.

Jaeger, R., 113.
Jellinek, K., 53.
Jona, M., 1.
Joos, G., 74, 116, 117.
Jung, G., 49, 57, 58, 61.

Kallmann, H., 16.
Keesom, W., 66, 101.
Kossel, 79, 80.
Krishnan, K. S., 14, 122.
Kuhn, W., 64.

Landé, A., 109, 112, 113, 114.
Lange, L., 24, 105.
Langevin, P., 47, 48, 120.
Lapworth, 90, 91, 99.
Laski, G., 51.
Lautsch, W., 58.
Leiser, R., 123.
Liebisch, 113.
Lindemann, 50.
Longchambon, L., 51.
Lucas, R., 51.

Mahanti, P. C., 14.
Maske, F., 59.
Meerwein, 80, 82.
Meisenheimer, J., 35.
Meyer, L., 65, 120, 126.
Montfort, 80.
Morgan, S. O., 14, 27, 103.

Nichols, 113.

Obolensky, 53.
Olivier, 87.
Ostwald, W., 87, 102, 103, 108.
Oxford, 90.

Petry, 95.
Philipps, B., 66.
Pol, van der, 25.
Potapenko, 53.
Preuner, G., 3.
Pungs, L., 3.

Raman, C. V., 14, 122.
Rao, R., 123, 124.
Reiche, F., 16.
Reis, A., 45.
Richter, 62, 65.
Robinson, 90, 91, 99.
Romanoff, 53.
Rubens, 103, 113, 116.

Sack, 25.
Sänger, R., 1, 2, 3, 58, 67.
Schaefer, C., 66.
Schaum, K., 51.
Scheel, K., 69.
Schleede, A., 49, 57, 58, 61.
Schmidt, W., 113.
Schrödinger, E., 50.
Sherrill, M. L., 39, 103.
Sircar, S. C., 14.
Smedt, de, 66.
Smith, 90.
Smyth, C. P., 14, 27, 47, 103.
Starke, 113.
Steiger, O., 2, 3, 6.
Stern, O., 16.
Stranathan, V. D., 23, 24, 103.
Stuart, H. A., 2, 6, 13, 58, 62, 67, 122, 123, 127.

Tammann, G., 51.
Thomson, J. J., 27, 29, 30.

Vorländer, 69, 89, 90, 91, 99.

Wagner, G., 62.
Walden, P., 25, 27, 33, 103, 127.
Walle, van de, 33.
Watson, H. E., 2.
Weissenberg, K., 20, 21, 45, 68.
Williams, J. W., 13, 14, 30, 32, 41, 103, 125.
Wohlwill, 21.
Wolf, K. L., 7, 61, 65, 95, 119, 120, 126.
Wrede, E., 17.

Zahn, C. T., 2.
Zocher, H., 64.

SUBJECT INDEX

Absorption spectra of di-substituted benzene derivatives, 95–99.
Alternating induced polarities, 88–91, 99.
Ammonia, structure of, 74.
Anharmonic vibrations, 56, 61.
Anisotropy of molecular field, 55.
Association, 5, 7, 8, 50, 55, 64, 65, 74, 86, 102.
—, chain/59, 65.
—, dipolar molecular, 101, 102, 107.
—, non-dipolar molecular, 101, 102, 106, 107.
—, temperature variation of, 105.
—, values of, 103.
Associations, molecular, 101–108.

Benzene derivatives, absorption spectra of di-substituted, 95–99.
— —, dipole moments of di-substituted, 28, 29, 119.
Benzene ring, structure of, 31.
Benzidine, structure of, 32.
Benzil oximes, isomeric, 35.
Benzophenone, polarization of, 59.
Binary liquid mixtures, polarity in, 101, 104, 106–108.
—, temperature effect, 108.
Born and Landé's equation, 113.

Carbon tetrachloride, structure of, 75.
Chain association, 59, 65.
Chain effect, 86, 87.
Chloroiodo-ethylenes, isomeric, 33, 34.
Cis-trans isomerism, 33–37, 70, 71.
Clausius-Mosotti theory, 110.
Complexes, formation of, 80.
Cyclohexane, structure of, 126.

Debye's dipole theory, 1, 2.
Debye's law, 2, 3, 6, 8, 11, 13, 14, 58.
Debye's X-ray method for measuring intra-atomic distances, 66.
Dekahydronaphthalenes, isomeric, 36.
Depolarization of scattered light, 44, 121, 124, 127.
— — and valency angle, 120.

Dichlorobenzenes, absorption spectra of, 96.
Dichloro-ethylenes, isomeric, 33, 34.
Dielectric constant and temperature, 1–14, 105.
—, data for chlorides, 9, 10.
— — ethers, 8, 9.
— — water, 7.
Dielectric constant of alcohols, possible ionic effects on, 25.
Dielectric constants of gases, 1–14.
— heterodyne method for, 3.
— infra-red term in, 11–13.
— measurement of, 7–10.
— — of liquids, 1.
Dielectric constants of heptane derivatives, 40.
Dihalogen compounds of ethylene, 41.
— of benzene, 41, 96.
Diphenyl, structure of, 31.
Dipoles, 7, 16, 30, 54, 55, 64, 79, 85.
Dipole moment, 11, 12, 13, 15, 16, 17 89.
— — and *cis-trans* isomerism, 33–37.
— — and duration of observation, 52.
— — and energy of activation, 84, 85.
— — and external electric field, 46–52
— — and internal field, 63, 82.
— — and intramolecular motions, 43–72.
— — and Kerr constant, 127.
— — and molecular structure, 27–37 39–41, 73–77.
— — and position of polar group i aliphatic compounds, 39, 40.
— — and substituents, 84.
— — and temperature, 60.
— — and velocity of reaction, 79–94.
— —, induced, 46, 47, 48, 49, 51, 52 53, 111, 120.
— —, natural, 44, 45, 46, 47, 48, 4 51, 61, 66, 70, 71.
— —, " rigid ", 44, 45, 46.
— — of alkyl chlorides, 9, 11, 13, 27.
— — of anisole, 60.
— — of benzophenone, 20.
— — of bromobenzene, 35.

Dipole moment of chlorobenzene, 31.
— — of cresols and cresylmethyl ethers, 30.
— — of dihalogen compounds of ethylene, 33, 34.
— — of diphenyl and derivatives, 20, 31, 32.
— — of di-substituted benzene derivatives, 28, 29, 119.
— — of ethers, 8, 11, 13, 20, 27, 30, 58, 67.
— — of ethyl bromide, 14.
— — of heptane derivatives, 39, 40.
— — of hydrocarbons, 27.
— — of iodobenzene, 35.
— — of methyl esters of aminobenzoic acids, 20.
— — of methyl esters of aminovaleric acids, 32.
— — of methyl iodide, 14.
— — of nitro-anisoles, 30.
— — of nitrobenzene, 124.
— — of *p*-bromoiodobenzene, 35.
— — of *p*-nitrochlorobenzene, 90.
— — of *p*-phenylenediamine, 32.
— — of pentaerythritol, 21.
— — of phenetole, 60.
— — of phenyl ether, 20.
— — of quinol diacetate, 29, 30.
— — of quinol diethyl ether, 29, 30, 59, 60.
— — of terephthalic acid esters, 29, 30.
— — of trichlorobenzene and trinitrobenzene, 31.
— — of water, 7, 10.
— — , molecular-beam method for, 15–21, 46, 51, 52, 56, 58, 61.
Dipole moments, vector addition of, 27, 90, 91, 119, 120, 125.
— — , in di-substituted benzene derivatives, 28, 29.
— — , deviations from, 30, 31, 95, 119, 120.
Dispersion curves, 51, 53, 54.
Displacement of electrons, 84, 85, 109.
— of ions, 109, 111, 114.
Dissociation constants of organic acids, 55, 79, 85, 86, 92.
Distortion, 31, 80, 83, 84, 87, 109.
Di-substituted benzene derivatives, absorption spectra of, 95–99.
— — dipole moments of, 28, 29, 119.

Electric moment, *see* Dipole moment.
Electrical opposites, theory of, 87.
Electronic polarization, 47, 117.
Electrons, displacement of, 84, 85, 109.
Energy of activation, 79, 86, 87.
— — and dipole moment, 84, 85.
— — and substitution in benzene nucleus, 87, 88, 89.
Energy of activation and velocity constant, 83, 84.
— — in removal of chlorine from substituted nitrochlorobenzenes, 92, 93, 94.
Equation of state, 4–7.
Equilibrium between several configurations of a molecule, 51, 53, 68.
Ethers, triangular structure of, 11.

Free rotation, 32, 54, 61, 62, 63, 66, 68, 71, 119, 120, 121.

Glutaric acids, 86, 87.
Group moments, 27, 62, 119.
— — of various substituents in aliphatic and in aromatic hydrocarbons, 28.
— — " positive " and " negative ", 29.

Heat of activation of maleic and fumaric acids, 71.
Hexahydro-terephthalic acids, isomeric, 35.
— — , halogen derivatives of, 36.
Homopolar compounds, 79, 80.

" Ideally uncoupled " molecules, 60, 62, 63, 71.
Induced dipole moment, 46, 47, 48, 49, 51, 52, 53, 111, 120.
Infra-red absorption bands, 10, 69.
Infra-red term in dielectric constants, 11–13.
Internal fields of molecules, 55, 59, 63, 66, 72, 82.
Internal vibrations of molecules, 45, 46, 47, 70.
— — and dipole moment, 43–72.
— — , amplitude of, 48.
— — , effect of temperature on, 56.
— — frequency of, 50, 53.
— — unsymmetrically anharmonic, 49, 52.
Intramolecular distances, 66, 86, 99.
— — Debye's X-ray method for, 66.
Ionization, frequency of, 79.
Ions, displacement of, 109, 111, 114.
— polarization of, 111, 113.
Isobornyl chloride, racemization of, 81.

Kerr constant, 120–126.
— — and dipole moment, 127.
Kerr constant of aliphatic alcohols, 125.
— — of normal saturated hydrocarbons, 125.
— — of paraldehyde, 126.
Kerr effect, 47.
— — and molecular structure, 119–127.
— — and valency angle, 120.

Liquid crystals, 64.

Magnetic moments of atoms, 16.
Maleic and fumaric acids, velocity of thermal transformation of, 71.
Mesomorphic phases, 64.
Methane, structure of, 75.
Methyl esters of aminovaleric acids, structure of, 32.
Molecular associations, 101–108.
Molecular-beam method for investigating polarity, 15–21, 46, 51. 52, 56, 58, 61.
— — , Estermann's apparatus for, 17–19.
— — , quantitative results, 16, 21.
Molecular heats and internal vibrations, 69.
Molecular polarization, 2, 9, 11, 13.
Molecular refraction, 11, 12, 102.
— — of complex ions, 80.
Molecular spectra, 44.
Molecular structure, 43.
— — and dipole moments, 27–37. 39–4-, 73–77.
— — and Kerr effect, 119–127.
— — , changes due to experimental methods, 46.
Molecules, aperiodic motion of, 53.
— , electrical energy of, 48.
— , electrical symmetry of, 44, 46.
— , electrocentric, 46.
— , internal fields of, 55, 59, 63, 66, 72, 82.
— , internal vibrations of, *see* Internal vibrations.
— , moment of inertia of, 44, 66, 69.
— , normal state of, 45.
— , organized state of, 62, 63, 70, 72.
— , rotation of, 52, 56.
— , thermal vibrations of, 53.
— , uncoupled state of, 70, 72.
Moment of inertia of molecules, 44, 66, 69.

Natural dipole moment, 44, 45, 46, 47, 48, 49, 51, 61, 66, 70, 71.
Nitro-anisoles, absorption spectra of, 97.
Nitrophenols, absorption spectra of, 98.
Non-polar substances, 17, 115.
— — in non-polar media, 106, 107.
— — , Kerr constants of, 123.
— — , polar substances dissolved in, 23.

Optical isomers, 76, 77.
Ortho-effect, 91, 92, 95, 98.

Paraldehyde, dipole moment and Kerr constant of, 126.
Pentaerythritol, 20, 21.
— , derivatives of, 21, 68.
Polar groups, angles between, 48.
Polar substances, 11, 16, 17, 45, 47, 48, 115.
— — in non-polar media, 23, 107.
— — in polar media, 107.
— — , Kerr constants of, 123.
Polarizability of ethers, 30.
— of ions, 73, 74.
— of molecules, 17, 21.
— of oxygen atom, 30.
— , axis of maximum, 122, 124, 125, 126, 127.
Polarity in binary liquid mixtures, 101, 104.
Polarization along the chain, 55, 64.
— , anisotropic, 48.
— , atomic, 47, 115–117.
— due to internal vibrations, 46.
— , electronic, 47, 117.
— , molecular, 2, 9, 11, 13.
— of ions, 111, 113.
— , optical, 11, 12.
— , orientation, 44, 46, 47, 49, 50, 52, 55, 56, 58, 72.
— — , effect of thermal motions on, 59.
— — , induced, 48.
— , radical, 45, 47.
— , total, 40, 102.
— , variation with concentration, 23–25.
— , variation with temperature, 23–25, 49, 50, 51, 58, 63.
Polarization-concentration curves, 23–25, 104.
— — compared with vapour pressure and viscosity curves, 106, 107.
Pyramidal structure of ammonia, 74.
— — of substances of type Ca_4, 20, 21.

Quadrupole moment, 75.
Quantum mechanics and molecular configuration, 73, 75, 76.
Quinols, isomeric, 36.

Racemization, velocity of, 77.
Refraction, atomic, 102.
— , molecular, 11, 12, 80, 102.
Refractive index and dielectric constant of regular crystals and Born and Landé's coefficient of repulsion, 109–114.
Relaxation times, 53.
Rotation of molecules, 52, 56.
Rotational quantum numbers, 16.
Rotatory vibrations of large molecules, 50.

" Screening ", 85, 93.
Solvents, effects, due to, 81, 99.
Steric hindrance, 93.
Stereochemical ideas, 43, 61, 62, 63, 71.
— , deviations from, 66, 68.
Structure of ammonia, 74.
— — benzene ring, 31.
— — benzidine, 32.
— — carbon tetrachloride, 75.
— — cyclohexane, 126.
— — ethers, 11.
— — methane, 75.
— — substances of type $C\alpha_4$, 20, 21.
— — water, 10, 30, 74.
Substances of type $C\alpha_4$, 52, 54, 61, 62, 65, 66, 67, 71.
— — , central symmetry of, 62, 65, 68.
— — , pyramidal structure of, 20, 21.
— — , tetrahedral structure of, 20, 21, 62, 68.
— — , variation of dipole moment with temperature, 62.
— — , Weissenberg's theory for, 20, 21, 45.
Substituents, negativing, 87.

Temperature and dielectric constants, 1–14, 105.
— and internal vibrations of molecules, 56.
Temperature-pressure curves for ethers and alkyl chlorides, 5, 6.
Tetrahedral structure of methane, 75.
— — of substances of type $C\alpha_4$, 20, 21, 62, 68.

" Uncoupling ", 50, 60, 61.

Valency angle, 55, 66, 67, 75, 120.
— — and depolarization of scattered light, 120.
— — and Kerr effect, 120.
— — in dichloromethane and carbon tetrachloride, 67.
— — in oxygen atom, 30, 31, 32, 36, 125.
van der Waals' equation, 4.
— — , deviations from, 4.
— — forces, 59, 101, 102.
Vector addition of dipole moments, 27, 28, 29, 90, 91, 119, 120, 125.
— — , deviations from, 30, 31, 95, 119, 120.
Velocity constant and energy of activation, 83.
Velocity of reaction and dipole moment, 79–94.
Velocity of transformation of camphene hydrochloride, 81.

Water molecule, triangular structure of, 10, 30, 74.